Indiana Water Resources Research Center
Annual Technical Report
FY 2010

Introduction

Overview: This report covers the activities of the Indiana Water Resources Research Center (IWRRC) for the period March 1, 2010 to February 28, 2011 and is reported by Ronald F. Turco, Director of the center. The report is provided to meet requirements and obligations under the 104 (B) of the USGS water centers program. The objectives of the fiscal year 2010 program of the IWRRC have been: (1) to continue to engage the water community in the State of Indiana as related to water research and education with a major focus on the Wabash River and Wabash River Watershed Basin; (2) Along this lines we have develop a dedicated water community at Purdue University– the Purdue Water Community (http://www.purdue.edu/dp/water/about.php); (3) Was elected chair of the Purdue Water Community (4) Foster a research program that encompass several water issues related to emerging contaminants (pharmaceuticals, personal care products, nanomaterials) primarily focused on the Wabash River and in support of the projects aid in the development of grant submission for major equipment related to water quality; (5) continue to support an outreach program related to water and water quality (in particular rural water protection/safety) and (6) to strengthen interactions with State regulatory agencies and Federal Agencies via active participation in a series of well water protection education programs.

In the last year we have supported externally reviewed 104(B) projects, received an award for our work with our USDA-CSREES facilitation grant (EPI-Net.org), maintained a functional website (www.iwrrc.org) been involved in the development, submission and management of number of grant proposals. In terms of web resources we have finalized the digital library of most of our back issues of water center reports and made them available via the Purdue University Library at “IWRRC Technical Reports”(http://docs.lib.purdue.edu/watertech/). We have had a large number of requests for older project information and we think this will be a welcome addition. We are finalizing work on a CEAP grant that was funded four years ago and this has lead to a number of interactions and secondary projects. We continue to work with Cites of Lafayette West Lafayette, Indiana and the Wabash River Enhancement Corporation (WREC) to facilitate discussions on long-range planning for Wabash River Redevelopment. We have received a “bridging grant” to continue to work on a 319 effort entitled: Developing a watershed management plan (WMP) for the Middle Wabash-Little Vermillion Basin (HUCs 05120108-010, 05120108-020, and 05120108-030) until three year funding for the implementation portion of the project arrives in Fall 2011. We continue to work with the “Wabash River Research Consortium” which is an effort to organize research on the Wabash River. We have also been active in establishing the Purdue University water community (PWC) and have facilitated a number of campus wide meetings to engage this group. We are currently developing a strategic plan for the PWC that includes interactions with the IWRRC. International, we are now working with Purdue’s office of global engineering on a number of water projects and have help facilitate work with Qatar.

For this reporting period, we continue the strategic outreach alliance with the Purdue Pesticide Program office for the development of document and educational materials on methods to prevent water contamination. By leveraging our funds with the Purdue Pesticide Program office’s core efforts we are using the opportunity to include the IWRRC in many of their programs. Our efforts have established a constant and vital outreach effort that is associated with prevention rather than remediation of environmental problems. In the future we are increasing our support of the PPP office. The recent title: Plan today for Tomorrow’s Flood: A flood response plan for Agricultural Retailers.

Project 01: Program Administration and State Coordination The administrative portion of the project has been used to support the management of the IWRRC's research projects and to facilitate the development of other research projects. We have also stepped up our efforts to coordinate campus level interactions (helping to create the Purdue Water Community) with state and federal agencies. All of these efforts have the ultimate goal of improving the quality of water resources in the State of Indiana. We have used a limited amount of money on the administrative portion but it has allowed the IWRRC director some means to invest time in the efforts to integrate with state and federal agencies. Most of IWRRC funds are used for projects and the director's time is contributed to the project. The IWRRC director has worked with state and federal environmental agencies, the governments of Indiana's cities and counties and key citizen groups on water education and water resources planning activities. In this way, the results from the research projects can be transferred to interested individuals in the state. The IWRRC director will participate in important national and international meetings related to water and environmental protection

Projects Areas 1. Continued work with the "State Water Monitoring Council". (https://engineering.purdue.edu/~inwater/conference/) leading to an online inventory of projects https://engineering.purdue.edu/~inwater/.

2. Work with community projects has continued including working with the Wabash River Enhancement Corporation (WREC) on a Volunteer Water Quality Monitoring project to allow opportunities for volunteer monitors to assess water quality conditions throughout the watershed. WREC and our partners conducted four Hoosier Riverwatch basic stream monitoring workshops with one workshop annually focused on training our volunteer monitors. Starting with two trainings courses offered spring of 2009, one in the spring of 2010, and one in the fall of 2010. Trained volunteers monitored stream quality at 10 stream sites entering their data in Hoosier Riverwatch's online database. The first Wabash Sampling Blitz occurred in September 2009 in concert with World Water Monitoring Day. During this and each subsequent spring and fall blitz, nearly 200 volunteers sampled 210 stream sites collecting water quality samples, measuring temperature and transparency in the stream, and photographing conditions present at the time of sampling. Sample filtering and analysis of samples with test strips also occurred either at staging locations or within the stream sample sites. In total, four sampling blitzes occurred during the grant period on September 18, 2009; April 9, 2010; September 17, 2010; and April 15, 2011. During each event, volunteer groups sampled three to four stream sites collecting field measurements for temperature and transparency, using test strips to analyze pH and nitrate at a minimum, and filling sample bottles for laboratory analysis of E. coli, nitrate+nitrite, orthophosphorus, and total organic carbon. Sample results were mapped by subwatershed drainage and posted to www.wabashriver.net as soon as possible following the event. In total 472 unique volunteers participated in the sampling blitzes. USEPA highlighted the Wabash Sampling Blitz in their Fall 2010 volunteer monitoring newsletter.

3. We have also continued working along with the Wabash River Enhancement Corporation, our partners, and education and outreach committees to provide numerous opportunities for watershed stakeholders to learn about the Wabash River and the Region of the Great Bend of the Wabash River watershed; facilitated education-based events; and coordinated programs to recognize the opportunities and commitments made by businesses and individuals throughout the watershed. Public meetings, the Clear-Blue-Green business certification program, field days, workshops, and the Wabash Sampling Blitz are just some of the activities used to educate our stakeholders.

4. The Wabash River runs some 764 km (475 mi), is situated across five 8-digit Hydrologic units (HUC), crosses 19 counties and at its full distance stretches from the Ohio border in the Northeast corner of the state to the Southwest corner where it combines with the Ohio River below Mount Vernon on its way to the Mississippi River. In the counties associated with the HUCs, the population is estimated at 2,388,658, fully one-third of the total population of the state. Working with Kent Wamsley from The Nature Conservancy (TNC) and Mark Pyron Ball State University we have established the Wabash River Research Consortium. This Wabash River Research Consortium is an extremely diverse group with representation from the Indiana Department of Natural Resources, Indiana Department of Environmental Management, Indiana State Department of Agriculture, NRCS, Fish and Wild Life, Purdue University, The Rivers Institute at Hanover College, Ball State University, DePauw University, The Wabash River Heritage Corridor Commission (WRHCC), Wabash River Enhancement Corporation (WREC) established by a grant from North Central Health Services; and IUPUI. Our goal is simple: develop a coordinated research and management agenda for

work on the Wabash River. The long-term goal of the effort is to help re-establish the Wabash River as a healthy water body that provides quality recreation and economic value to the state.

5. Continued to work with Dr. Fred Whitford and the Purdue Pesticides Program Office to establish an outreach effort centered on water protection emphasizing pesticide and farmstead management. We are undertaking efforts to enhance this interaction

6. Continued interactions with a number of consulting firms related to water quality issues.

Grant Applications Submitted thorough/with IWRRC: a. (Funded and ongoing) USDA-AFRI Tracking the survival and distribution of Mycobacterium avium subsp paratuberculosis in the agroecosystem. $375,000. E. Rizaman, C. Wu and R. Turco. b. (Funded and ongoing) SUNGRANTS: Optimization of biomass productivity and environmental sustainability for cellulosic feedstocks: Land capability and life cycle analysis. $875,000 S.M. Brouder, PI, R.F. Turco, J.J. Volenec, D.R. Smith and G. Ejeta CoPIs c. (Funded and ongoing) IDEM 319: Wabash River: Lafayette-West Lafayette Reach of the Wabash River Watershed Management Plan. Submitted in conjunction with the Wabash River Enchantment Corporation $700,000. L. Prokopy, L. Bowling, K. Wilson and R. Turco. i. Bridging grant approved for one year of additional support. d. (Funded and ongoing) USDA NRI, Managed Ecosystems. Ecological services of agro-biofuels: productivity, soil C storage, and air and water quality. $399,999. Submitted Dec. 2007. S.M. Brouder, PI, R.F. Turco, J.J. Volenec, D.R. Smith and G. Ejeta CoPIs. e. (Funded and ending) USDA Conservation Effects Assessment Program. $660,000. Watershed-Scale Evaluation of BMP Effectiveness and Acceptability: Eagle Creek Watershed, Indiana. Developed with Jane Frankenberg, Lenore Tedesco, Jerry Shively, Linda Prokopy. This was an outgrowth of an effort submitted last year to EPA but note funded: Creating sustainable drinking water supplies for Central Indiana: Innovations to achieve reductions in watershed and reservoir nutrient levels. f. (Continued Funding) USEPA $350,000. Fate of hormones in tile-drained fields and impact to aquatic organisms under different animal waste management practices. Linda Lee, S. Brouder, C. Jafvert, M. Sepulveda and R. Turco. g. (Continued Funding) IDEM-319 Development and Demonstration of Outcomes-Based Evaluation Framework for the Indiana Nonpoint Source Program. Developed with Jane Frankenberger, and Linda Prokopy. h. (Submitted) IDEM-319 $240,000 Region of the Great Bend of the Wabash River Implementation Project with S. Peel and R. Goforth i. (Submitted) NRCS-CIG: $210,000 Ramifications of soil management options for biofuel production on Soil Processes: implications to soil quality. j. (Not funded) USDA-AFRI: $20 M. CAP-ECO Mazie project. S. Brouder and 30 others. k. (Submitted) IDEM-319 $132,000 Deer Creek-Sugar Creek Watershed Management Plan and Implementation Program. Project with S. Peel and R. Goforth.

External Board of Advisors Membership: Dr. Lenore Tedesco, Director Center for Earth and Environmental Science, Indianapolis IN Dr. Jack Wittman, President, Wittman Hydrosciences, Bloomington IN Dr. Bill Guertal Director, USGS Indiana Water Science Center, Indianapolis IN Mr. Jeff Martin, USGS Indiana Water Science Center, Indianapolis IN Dr. Linda Lee, Associate Director Center for the Environment, Purdue University Faculty Advisory Committee: Dr. Linda Lee, Professor and Director of ESE Dr. Jane Frankenberger, Agriculture and Biological Engineering Dr. Larry Nies, Civil and Environmental Engineering Dr. Inez Hua, Civil and Environmental Engineering

Research Program Introduction

None.

Nutrient and carbon delivery to streams in artificially drained landscapes of the Midwest: matrix flow, overland flow or macropore flow?

Basic Information

Title:	Nutrient and carbon delivery to streams in artificially drained landscapes of the Midwest: matrix flow, overland flow or macropore flow?
Project Number:	2007IN227G
Start Date:	4/1/2008
End Date:	3/31/2011
Funding Source:	104G
Congressional District:	7
Research Category:	Ground-water Flow and Transport
Focus Category:	Solute Transport, Surface Water, Hydrology
Descriptors:	
Principal Investigators:	Philippe Gilles Vidon, Nancy T. Baker, Jeffrey W Frey

Publications

1. Cuadra, P.E., P. Vidon, 2009. Natural Variability in Dissolved Organic Carbon and Dissolved Organic Nitrogen Transport in Artificially Drained Landscapes of the U.S. Midwest. Abstract#B34A-04. American Geophysical Union Joint Assembly, Toronto, ON, Canada, May 2009
2. Cuadra, P.E., P. Vidon, 2009. Natural Variability in Dissolved Organic Carbon and Dissolved Organic Nitrogen Transport in Artificially Drained Landscapes of the U.S. Midwest. Abstract#B34A-04. American Geophysical Union Joint Assembly, Toronto, ON, Canada, May 2009
3. Vidon, P. and P.E. Cuadra*, 2010. Impact of precipitation characteristics on soil hydrology in tile-drained landscapes. Hydrological Processes, DOI: 10.1002/hyp.7627 (Online – Early View).
4. Cuadra*, P.E., and P. Vidon. Storm nitrogen dynamics in tile-drain flow in the US Midwest. Biogeochemistry (in review).
5. Vidon, P., and Cuadra*, P.E. Phosphorus dynamics in tile-drain flow during storms in the US Midwest. Agricultural Water Management (in review).
6. Cuadra, P.E., P. Vidon, 2009. Natural Variability in Dissolved Organic Carbon and Dissolved Organic Nitrogen Transport in Artificially Drained Landscapes of the U.S. Midwest. Abstract#B34A-04. American Geophysical Union Joint Assembly, Toronto, ON, Canada, May 2009
7. Vidon, P. and P.E. Cuadra*, 2010. Impact of precipitation characteristics on soil hydrology in tile-drained landscapes. Hydrological Processes, DOI: 10.1002/hyp.7627 (Online – Early View).
8. Cuadra*, P.E., and P. Vidon. Storm nitrogen dynamics in tile-drain flow in the US Midwest. Biogeochemistry (in review).
9. Vidon, P., and Cuadra*, P.E. Phosphorus dynamics in tile-drain flow during storms in the US Midwest. Agricultural Water Management (in review).

Progress Report for Award # 08HQGR0052 - Nutrient and carbon delivery to streams in artificially drained landscapes of the Midwest: matrix flow, overland flow or macropore flow? – **YEAR 2**

04/08-04/11, (PI) P. Vidon, (Co-PIs) J.W. Frey, N.T. Baker. USGS-NIWR National Competitive Grant Program (Award # 08HQGR0052). Title: Nutrient and carbon delivery to streams in artificially drained landscapes of the Midwest: matrix flow, overland flow or macropore flow? $129,042

Abstract / Summary

Understanding the processes controlling the delivery of nitrogen, phosphorus and carbon to streams in artificially drained landscapes of the Midwest is of critical importance to developing comprehensive nutrient management strategies at the watershed scale. Most nutrient and carbon losses in artificially drained landscapes of the Midwest occur during precipitation events through tile drain flow and overland flow. In addition, recent research has identified preferential flow through soil macropores as an important export mechanism contributing to tile drain flow. There is nevertheless a lack of empirical data documenting the relative importance of overland flow (OLF), matrix flow (MF) and preferential flow through soil macropores (PF) on nitrogen, phosphorus and dissolved organic carbon (DOC) losses to streams. For this project, a team of USGS scientists has teamed up with the PI (Vidon) to measure the relative importance of OLF, MF and PF during 6-8 storms over a two-year period in an artificially drained Midwestern watershed, and to identify the changes in the nature of in-stream nitrogen (nitrate, ammonium, total Kjeldahl nitrogen (TKN)), phosphorus (soluble reactive phosphorus (SRP), total phosphorus (TP)), and DOC (aromaticity) during storms.

Fieldwork is taking place in a small first order watershed, which is continuously monitored by the U.S. Geological Survey as part of the National Water Quality Assessment Program (NAWQA) for the White River, Great, and Little Miami River Basins. Water quality data have been collected in precipitation and at 2-4 hour intervals during 7 storms in overland flow, tile flow and the stream. Data analysis is underway and the PIs will used a two phase (tile + stream) multi-tracer (chloride, cation, oxygen-18) approach to independently estimate the relative importance of tile drain flow, overland flow, precipitation and seepage in the stream, and the relative importance of matrix flow and preferential flow through soil macropores in tile flow. The potential of DOC and DOC specific UV absorbance (SUVA) as potential hydrologic tracers to identify water sources in a watershed context will also be evaluated.

By providing a direct quantification of the relative importance of each water delivery pathway to NPC transport to streams for a variety of storms and crop development conditions, data collected as part of this project provide an increased understanding of the processes controlling NPC delivery to streams, and provide tools to better target best management practices (BMP) to minimize the impact of agriculture on raw rural water quality in the Midwest.

Problem

Phosphorus, nitrogen and carbon losses to streams affect aquatic productivity, food web structure, and water quality (Martin et al., 1999; Dalzell et al., 2005). Understanding the processes controlling the delivery of these solutes to streams is therefore of paramount importance in order to develop comprehensive watershed nutrient management strategies.

It is well established that most nutrient exports occur during episodic high flow periods (Royer et al., 2006) and that nutrient concentration in streams, hydrological processes and flowpaths often change rapidly during precipitation events in response to variations in precipitation intensity/duration and pre-event moisture conditions (Creed and Band, 1998; Sidle et al., 2000; Hangen et al. 2001; Wigington et al. 2003; Inamdar et al., 2004). The nature of dissolved organic carbon (DOC) (aromaticity, relative abundance of humic/non-humic substances) in streams also often varies during storms, indicating a change in the sources of DOC as a function of discharge (Katsuyama and Ohte, 2002; Hood et al 2006).

High nutrient losses and quick changes in nutrient and carbon concentration/nature during storms stress the importance of conducting research aimed at thoroughly understanding nutrient dynamics and flowpaths during storms. This will increase our ability to predict nutrient and carbon losses at the watershed scale with more precision in the years to come. It is especially important to address this issue in artificially drained landscapes of the Midwest, as agricultural states like Indiana, Ohio and Illinois have been identified as major contributors to excess nutrients in the Mississippi River (Goolsby et al., 2000; Royer et al. 2006).

Recent research has identified preferential flow through soil macropores as an important transport mechanism for solute transport during precipitation events in artificially drained landscapes of the Midwest (Kung et al., 2000a; Stone and Wilson, 2006). Nutrient losses via overland flow in artificially drained landscapes have also been shown to influence the dynamics of NPC losses to streams (Kurz et al., 2005; Royer et al., 2006). Nevertheless, there is a dearth of empirical data documenting the relative importance of overland flow (OLF), matrix flow (MF), and preferential flow through soil macropores (PF) during storms and/or the relative importance of each of these processes on the delivery of nutrients and carbon to streams in artificially drained landscapes of the Midwest.

Research Objectives

Primary objective 1: Identify the relative importance of overland flow, stream bank seepage, matrix flow and preferential flow through soil macropores to streamflow during storms in artificially drained landscapes of the Midwest.

Primary objective 2: Identify the relative importance of each of these water delivery pathways on nitrogen, phosphorus and carbon delivery to streams during storms. Particular attention will be given to characterizing the changes in the nature of N (nitrate, ammonium, total Kjeldahl nitrogen (TKN)), P (soluble reactive phosphorus (SRP), total phosphorus (TP)), and dissolved organic carbon (DOC) (aromaticity) losses to the stream during the storms studied.

Achieving these objectives will help manage raw rural water quality and quantity by allowing landscape managers to better target BMPs, as BMPs often influence soil moisture and water infiltration in soil, and therefore the relative importance of overland flow, matrix flow, and preferential flow through soil macropores. This broad objective is identified as an area of high priority in the RFP FY2007 of the Water Resources Research National Competitive Grant Program, section 104G (page 4).

Two corollary objectives will also be addressed as part of this project:

Corollary objective 1: By monitoring tile drain flow in two tile drains draining two fields under till and no-till, respectively, we will assess the impact of this best management practice (BMP) on raw rural water quality in the watershed.
Corollary objective 2: Assess the potential of using DOC and DOC Specific UV Absorbance (SUVA) to identify the relative contribution of various sources of water to the stream during storms. This objective will contribute to the development of better techniques to assess various components of the water cycle, which is a priority area for the 104G program in 2007 (RFP FY 2007, page 4).

Methodology

The project is field based in nature and is taking take place in the headwaters of Sugar Creek Watershed, in a small watershed (7.2 km^2), locally known as Leary Weber Ditch (LWD). Soils in LWD are suited for row crop agriculture such as corn and soybeans but require artificial drainage to lower the water table, removing ponded water, adding nutrients and ensuring good soil tilth. LWD is representative of many watersheds in the Midwest where poorly drained soils dominate and where artificial drainage is commonly used to lower the water table.

For this project, we quantified water and nutrient fluxes and delivery pathways in LWD for a total of 7 storms in years 1 and 2. These storms varied in duration and intensity and 3 of them generated significant amounts of overland flow. For each storm, a stream water mass balance will be performed (in progress). This approach will allow the team of PIs to identify the relative contribution to discharge of overland flow, tile flow, stream bank seepage, and direct interception of precipitation by the stream. Hydrological tracers (cation, oxygen-18, chloride) will be used to differentiate the relative contribution of new water (event water) and old water (pre-event water) to the stream during each storm, and to differentiate the relative importance of new water and old water in tile drain flow. In tile drains, old water will be considered equivalent to matrix flow (MF) and new water equivalent to preferential flow through soil macropores (PF) (Stone and Wison, 2006). Nitrogen (nitrate, ammonium, total Kjeldahl nitrogen (TKN)), phosphorus (soluble reactive phosphorus (SRP), total phosphorus (TP)) and dissolved organic carbon (DOC) will be measured in overland flow, tile drain flow, streamflow and precipitation to identify the relative importance of each water delivery pathway to nutrient and carbon losses to the stream. The change in the nature of DOC during each storm will be monitored spectrometrically to determine the usability of DOC as a tracer and characterize changes in the sources of DOC to the stream during storms.

Results

Analysis of data for the whole watershed is currently underway. However, three manuscripts looking at water, N and P dynamics in tile drains only (for now) are in various stages of publication (See list below). A summary of the findings presented in these manuscripts is shown here.

In spring, although variations in antecedent water table depth imparted some variation in tile flow response to precipitation, bulk precipitation was the best predictor of mean tile flow, maximum tile flow, time to peak and runoff ratio. The contribution of macropore flow to total flow significantly increased with precipitation amount, and macropore flow represented between 11% and 50% of total drain flow, with peak contributions between 15% and 74% of flow. For large storms (>6 cm bulk precipitation), cations data indicated a dilution of groundwater with new water as discharge peaked. Although no clear dilution or concentration patterns for Mg^{2+} or K^{+} were observed for smaller tile flow generating events (<3 cm bulk precipitation), macropore flow still contributed between 11% and 17% of total flow for these moderate size storms.

Bulk precipitation amount had little impact on solute median concentrations in tile-drains during storms, but clearly impacted NO_3^- concentration patterns. For large storms (> 6 cm of bulk precipitation), large amounts of macropore flow (43-50% of total tile-drain flow) diluted NO_3^- rich groundwater as discharge peaked. This pattern was not observed for NH_4^+ and DON or for smaller tile-flow generating events (< 3cm) during which macropore flow contributions were limited (11-17% of total tile-drain flow). Precipitation amount was positively ($P<0.01$) correlated to NO_3^- and NH_4^+ export rates, but not to DON export rates. Limited variations in antecedent water table depth in spring had little influence on N dynamics for the storms studied. Although significant differences in flow characteristics were observed between tile-drains, solute concentration dynamics and macropore flow contributions to total tile-drain flow were similar for adjacent tile-drains. Generally, NO_3^- represented >80% of N load during storms, while DON and NH_4^+ represented only 2-14% and 1-7% of N load, respectively.

Depending on the storm, median concentrations varied between 0.006-0.025 mg/L for SRP and 0.057-0.176 mg/L for TP. For large storms (> 6 cm bulk precipitation), for which macropore flow represented between 43-50% of total tile-drain flow, SRP transport to tile-drains was primarily regulated by macropore flow. For smaller tile-flow generating events (<3 cm bulk precipitation), for which macropore flow only accounted for 11-17% of total tile-drain flow, SRP transport was primarily regulated by matrix flow. Total P transport to tile-drains was primarily regulated by macropore flow regardless of the storm. Soluble reactive P (0.01-1.83 mg/m^2/storm) and TP (0.10-8.64 mg/m^2/storm) export rates were extremely variable and positively significantly correlated to both mean discharge and bulk precipitation. Soluble reactive P accounted for 9.9-15.5% of TP fluxes for small tile-flow generating events (<3 cm bulk precipitation) and for 16.2-22.0% of TP fluxes for large precipitation events (>6 cm bulk precipitation). Although significant variations in tile-flow response to precipitation were observed, no significant differences in SRP and TP concentrations were observed between adjacent tile-drains.

Major Conclusions and Significance

Results presented above significantly increase our understanding of the hydrological functioning of tile-drained fields in spring, when most N losses to streams occur in the US Midwest. In particular, results stress the non-linear behavior of N export to tile drains during spring storms in artificially drained landscapes of the US Midwest, at a critical time of the year for N management in the MRB. For P, results stress the dominance of particulate P and the importance of macropore flow in P transport to tile-drains in the US Midwest. This brings critical insight into P dynamics in tile-drains at a critical time of year for water quality management.

Publications (* = graduate students)

Vidon, P. and P.E. Cuadra*, 2010. Impact of precipitation characteristics on soil hydrology in tile-drained landscapes. *Hydrological Processes*, DOI: 10.1002/hyp.7627 (Online – Early View).

Cuadra*, P.E., and P. Vidon. Storm nitrogen dynamics in tile-drain flow in the US Midwest. *Biogeochemistry* (in review).

Vidon, P., and Cuadra*, P.E. Phosphorus dynamics in tile-drain flow during storms in the US Midwest. *Agricultural Water Management* (in review).

Presentations

Vidon, P, P.E. Cuadra*, 2010. Phosphorus dynamics in tile-drain flow during storms in the US Midwest. Annual meeting of the American Water Resources Association, Philadelphia, PA, November 2010 (Forthcoming)

Hennessy*, M, P. Vidon, 2009. Constraining nitrogen, phosphorus and carbon exports in a Midwestern Agricultural Watershed. American Geophysical Union Joint Assembly, Abstract#H71B-07. page 5, Toronto, ON, Canada, May 2009.

Cuadra*, P.E., P. Vidon, 2009. Natural Variability in Dissolved Organic Carbon and Dissolved Organic Nitrogen Transport in Artificially Drained Landscapes of the U.S. Midwest. Abstract#B34A-04. Page 103, American Geophysical Union Joint Assembly, Toronto, ON, Canada, May 2009.

Grant Submissions n/a

Students

Graduate students: 3
Undergraduate Researchers: 4

Local and Regional Assessment of Biofuel Production Facilities Impacts on Freshwater Quality in Indiana

Basic Information

Title:	Local and Regional Assessment of Biofuel Production Facilities Impacts on Freshwater Quality in Indiana
Project Number:	2010IN219B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	4
Research Category:	Water Quality
Focus Category:	Models, Water Quality, Water Quantity
Descriptors:	
Principal Investigators:	Suresh Rao, Suresh Rao

Publications

There are no publications.

Local and Regional Impacts of Biofuel Production Facilities on Freshwater Quantity and Quality in Indiana

Report as of FY2010 for 2010IN219B

Publications

Project 2010IN219B has resulted in no reported publications as of FY2010.

Report Follows

IWRRC 2010 Project Report

State: IN **Project Number:** 2010IN219B
Title: Local and Regional Impacts of Biofuel Production Facilities on Freshwater Quality in Indiana
Project Type: Research
Focus Category: MOD, WQL, WQN, WU
Keywords: Freshwater availability; blue and green water; water use; biofuel; water quality
Start Date: 3/01/2010 **End Date:** 2/28/2011
Congressional District: 4 **PI:** P. Suresh C. Rao **email**:pscr@purdue.edu

Abstract / Summary
Freshwater plays a crucial role in all stages of biofuel production - from biomass cultivation through its conversion into biofuel. Corn ethanol production increases may further compromise water quality and compete with other sectors of freshwater use (e.g., urban and industrial). The effects of expanded biofuel production on freshwater, a limited but a renewable natural resource, need to be considered as demand for freshwater from various sectors increases and places additional stress on already constrained freshwater supplies. An increase in corn cultivation using current intensive agricultural practices will also impair water quality as a result of the runoff of fertilizer and pesticides into surface water and groundwater. Moreover, biorefineries also discharge wastewater containing several inorganic and organic contaminants that could impair surface-water quality and compound the problem on already impaired freshwater. Therefore, both quantity and quality of freshwater should be considered when assessing the impacts of biofuels production expansion on local and regional freshwater. The water use regime, originally proposed by Weiskel et al. (2007), is adopted for this research and modified to take into account water quality impacts by non-point sources in addition to quantity on the degree of human influence on region's hydrology. The *criticality ratio* is also combined as a method of determining water stress. Eight watersheds (HUC-8), within which biorefineries are currently in operation and are located within the band of mid-northern part of Indiana, were selected for an evaluation of shifts in "water-use regimes". Our analysis shows that, at the *watershed scale,* the consumptive water uses from various major sectors are small under average weather conditions. This evaluation, however, changes dramatically when *water-quality impairments* are taken into account; all watersheds we evaluated would be judged to be under severe water stress. Moreover, under *drought conditions*, all watersheds we examined would be judged to be under severe stress both from quantity and quality perspectives. Competing demands for freshwater are most likely to be experienced at spatial scales smaller than a watershed scale. This is especially important since freshwater withdrawals are from groundwater sources, but return flows are to surface water (streams). Thus, continued depletion by increasing pumping from aquifers can, over time, result in significant water stress conditions. Freshwater use data we utilized in our analysis came from the USGS reports which are published once every five years, and are available aggregated only at the county level. We did not access data that might be available with the local authorities who issue permits for groundwater use. Our assessments would be enhanced if such local-scale data were used to generate the water regime plots, and these plots would be even more useful to local water managers. Hydro-climatic shifts projected climate change [increased frequency of extreme events] would increase the likelihood of water-stress in the watersheds.

Statement of Critical Regional/State Freshwater Problem

The annual bioethanol production capacity in the United States has increased rapidly and reached 55 billion liters as of January 2009. Indiana, a major contributor to this trend, is the sixth highest bioethanol producing state (RFA 2010). Water plays a crucial role in all stages of biofuel production - from cultivation of feedstock through its conversion into biofuel (Aden 2007). The National Research Council (Hill et al. 2006) and other studies (Donner and Kucharik 2008) have warned that the corn ethanol production increases may further compromise water quality and compete with other sectors of water use (e.g., urban and industrial).

Freshwater is a limited, but a renewable natural resource, and many parts of the world or even the United States are already experiencing water scarcities. These scarcities are complicated by increasing demands of a growing population and economies. Moreover, as demand for water from various sectors increases and places additional stress on already constrained freshwater supplies, the effects of expanded biofuel production may need to be considered (GAO 2009). Although, total surface water withdrawals for Indiana did not show significant increasing trend over time, relatively large annual fluctuations have occurred (Indiana State 2008). Moreover, it is important to take into account the local or regional variability of water availability and also current and projected use trends. According to GAO's 2003 survey, Indiana was among the states which, under average water conditions, that are likely to experience water shortages in one or more localized areas within 10 years from the surveyed year (GAO 2003). Some communities have become concerned that freshwater withdrawals for biofuels production would have adverse impacts on their drinking water and municipal supplies, and are pressuring states to limit water use by bioethanol facilities. For example, at least one Minnesota local water district denied a permit for a proposed biorefinery based on concerns about limited water supply in the area (GAO 2009).

An increase in corn cultivation using current agricultural practices will also impair water quality as a result of the runoff of fertilizer and pesticides into surface water and groundwater, leading to impacts at the scales of the entire Mississippi River Basin and the Gulf of Mexico (e.g., Donner et al. (2004) and Donner and Kucharik (2008)). Fertilizer runoff can lead to nutrient enrichment, harmful algal blooms, decreased water clarity, and anoxia in the water, all of which impair aquatic habitats. The application rates of atrazine, a commonly used herbicide for corn production, are highest in the Corn Belt, and it was also the most widely detected pesticide in watersheds in this area (Capel and Larson 2001). Moreover, biorefineries also discharge wastewater containing several inorganic and organic contaminants that could impair surface water quality (Schnoor et al. 2008). However, the type of contaminants discharged varies by the type of biofuels produced and the biomass conversion technology used. For example, ethanol biorefineries generally discharge chemicals or salts that build up in cooling towers and boilers or are produced as waste by reverse osmosis, a process used to remove salts and other contaminants from water prior to discharge from the biorefinery. In contrast, biodiesel refineries discharge other pollutants such as glycerin that may be harmful to water quality (GAO 2009).

According to Indiana Department of Environmental Management (IDEM), Indiana's water bodies have already been highly impaired in terms of organic compounds (rank 1 among U.S. states) and biological community (rank 7), and that this situation is likely to only increase (Indiana State 2010). Although, there is multitude of sources for freshwater contamination, the increase of biofuels production will compound the problem because biorefineries produce wastewater with high concentration of organic and inorganic constituents and they require high amount of freshwater use. New source of freshwater (most likely, groundwater) is required to treat or dilute the contaminated effluents from biofuels production process. Therefore, both quantity and quality of freshwater should be considered when assessing the impacts of biofuels production expansion on local and regional freshwater.

Related Research

There have been several efforts to estimate water use for biofuel production. Gerbens-Leenes et al. (2009) estimated the water footprint (WF) of bioenergy from 12 crops that currently contribute the most to global agriculture production. Although, they had calculated the WF of each crop by country and bioenergy to be produced, this study is focused only on the agricultural (biomass) production stage. To overcome the limitations of prior studies, which had not accounted for the varied regional irrigation practices on estimating the water requirement for bio-ethanol production, Chiu et al. (2009) used regional time-series data for agricultural and ethanol production in the U.S. to estimate state-level field-to-pump water requirement of bioethanol across the nation. They estimated the embodied water in ethanol by state and evaluated the local impacts in terms of groundwater withdrawal caused by bio-ethanol production; however, they only considered the corn ethanol industry even when projecting the expansion of the biofuels industry.

Data Analysis & Technical Approach

Since most of the studies have been done at a large scale, global or national, and are highly focused on feedstock growth, this study aims to investigate local and regional impacts of freshwater use and wastewater discharges, especially from biofuel conversion processes. Indiana, in USDA farming Region 5, does not use much irrigation water for feedstock cultivation compared to other Regions, which means changing or increasing feedstocks production will not have much impact on freshwater withdrawals. Therefore, freshwater uses in biorefineries for biomass conversion will have relatively high potential to introduce local- or regional-scale conflicts for competing uses and quality impairment. Thus, water required for biomass conversion facilities will especially be highlighted in this research. While freshwater uses for biofuels conversion processes have local impacts on water problems, the discharge of wastewater effluents from those facilities have potential to expand the scale of the problem to region or interstate levels. However, wastewater quality from biorefineries has not been investigated.

The methods used to determine the appropriateness of bioethanol plant locations in Indiana follow those outlined by Weiskel et al. (2007). The method is briefly explained below, and the reader is referred to Weiskel et al. (2007) for more detailed explanation. In this study, a water-use regime is created for each watershed containing a bioethanol plant. The water use regime is defined by considering the water balance of a bounded watershed.

$$P + (GW_{in} + SW_{in}) + H_{in} - \Delta S/\Delta t = ET + (GW_{out} + SW_{out}) + H_{out} \tag{1}$$

where P is precipitation; $(GW_{in} + SW_{in})$ is groundwater and surface water inflows; ET is evapotranspiration; $GW_{out} + SW_{out}$ is groundwater and surface water outflows; H_{in} is total return flow to the control volume from all sources, including return flows from local withdrawals and imported withdrawals; H_{out} is withdrawals from the control volume; and $\Delta S/\Delta\mathrm{t}$ is the rate of change in control volume storage (surface and subsurface). All units are volume/time (L^3/T).

Although, Weiskel et al. (2007) recommended consideration of stream basins and aquifers separately, it is assumed here that the change of net storage in aquifer is negligible when averaged over the period of interest, which implies $GW_{in} \approx GW_{out}$. Thus, overall water balance is mainly determined by the change of surface water flow. This assumption is feasible because, in Indiana, most of the water demand in agricultural sector, which generally is the major source for local freshwater demand, is known to be fulfilled by rainfall and the irrigation rate from groundwater is relatively low (Wu et al. 2009). Therefore, only the water balance for stream basin is explicitly evaluated for this study. In this case, the total water balance can be rewritten as:

$$P + SW_{in} + H_{in} - \Delta S/\Delta t = ET + SW_{out} + H_{out} \tag{2}$$

The net basin flux (NetFlux), which may be directly available for human use can be derived by rearranging the Eq. (2).

$$\begin{aligned} NetFlux &= (P - ET) + SW_{in} + H_{in} - \Delta S/\Delta t \\ &= SW_{out} + H_{out} \end{aligned} \tag{3}$$

According to Eq. (3), two different forms can be used to obtain net flux depending on the data available. When the latter form of net flux is used, only two data sets, outflow of surface water and human water withdrawal, are required and those are typically available.

When considering water quality issues, the quantity that is hypothetically imported into the closed basin (W_{dilute}) to dilute the contaminated surface water should be added to the net flux. Thus, the latter form of Eq. (3) is rewritten as:

$$NetFlux = SW_{out} + H_{out} + W_{dilute} \tag{4}$$

All terms in the water balance are normalized by dividing each term by the net system flux, which yields normalized human inflow (h_{in}) and outflow (h_{out}). Eq. (3) is used for estimating h_{in} and h_{out} without considering the water quality issue, while Eq. (4) is used when water quality is considered.

$$h_{in} = H_{in}/NetFlux \tag{5}$$

$$h_{out} = H_{out}/NetFlux \tag{6}$$

Plotting h_{in} versus h_{out} [calculated by Eq. (5) and (6)] for each watershed yields the water use regime. The target for water use intensity is a one-to-one ratio of h_{in} to h_{out}, or the 45° line that is seen on the graphs shown in the Result section. This line represents a state in which imports = exports, although the water returned is not necessarily of the same quality as the water withdrawn. In the water regime plots, the region below the 1:1 diagonal line represents the "withdrawal regime" (i.e., withdrawals > imports), and the region below the diagonal represents the "import regime" (imports > withdrawals). Unsustainable freshwater withdrawals may arise either from large withdrawals or significant water quality impairment or both.

The derivation of the freshwater-use regime is useful for analyzing the intra-seasonal and geographic differences within and among watersheds. However, the water-use regimes demonstrate the degree of human influence on a region's hydrology and not necessarily the water stress that results from such a condition. An objective measure must be derived to assess the relative water stress implied by a given watershed's water use regime. The criticality ratio – defined by Alcamo et al. (2000) as the ratio of water use to water availability – is used as a method of determining water stress. The levels of water stress are defined below:

- 0 – 0.1: no stress
- 0.1 – 0.2: low stress
- 0.2 – 0.4: mid stress
- 0.4 – 0.8: high stress
- 0.8 – 1: very high stress

These criticality ratios can be directly applied to the water use regime. In the modified water use regime described above,

$$h_{out} = \frac{H_{out}}{NetFlux} \tag{7}$$

The criticality ratio is defined as:

$$\frac{water\ use}{water\ availability} = \frac{H_{out}}{(P - ET) + SW_{in} + H_{in} - \Delta S/\Delta t} = \frac{H_{out}}{NetFlux} = h_{out} \tag{8}$$

The above levels of water stressed defined by the criticality ratio can easily be included in the water use regime.

After deriving the water-use regime for each watershed, a worst-case scenario was examined to explore issues that may result in the inappropriateness of a certain location for ethanol production. Returning to the USGS stream flow measurement data, the discharge rate at the lower fifth percentile of all years was used in place of the mean discharge rate to re-calculate the water use regime. This reveals the main problem inherent with drought years: a much greater amount of water input is required to dilute harmful chemicals to acceptable levels. The water-use regimes were re-calculated using the twenty-fifth percentile of discharge data to demonstrate the effects of less extreme drought years.

Indiana Watersheds Evaluated

The freshwater use regime is constructed for the HUC-8 watersheds in which bioethanol plants are in operation to compare how freshwater use by biofuels production impacts local hydrologic stress. As of December 2010, Indiana had 12 completed ethanol plants and one more under construction (Figure 1). The combined ethanol production of the plants completed and the additional one under construction will exceed 1.1 billion gallons per year, which represents 7% of the U.S. ethanol industry (ISDA 2010). The biorefineries are located close to each other, and therefore conflicts over water use are likely to occur. Corn-based ethanol production with the nameplate capacities of 150 to 415 million liters typically requires feedstocks to be supplied from regions that stretch several tens of miles of radius from a plant's location. While production process itself may induce local conflicts over freshwater use, the spatial range of impact caused by feedstock production can be expanded far beyond the scale of county and even of a watershed. Thus, among the Indiana biorefineries, nine located in eight watersheds within a similar hydro-geologic region were selected (Table 1).

Table 1. Selected watersheds for the construction of water use regime.

Watershed	Total Area (km^2)	Crop (Corn) Area (km^2)	Biorefinery	Production Capacity (MG/year)
(A) Iroquois	2,208	902	Iroquois Bio-energy	40
(B) Eel (Upper)	2,112	1,313	POET Biorefining – North Manchester	65
(C) Middle Wabash Deer	1,731	1,259	The Andersons	110
(D) Upper Wabash	4,229	922	Indiana Bio-Energy	110
(E) Mississinewa	2,114	577	Central Indiana Cardinal Energy	40 100
(F) Salamonie	1,450	1,037	POET Biorefining - Portland	65
(G) Upper White	7,044	1,506	POET Biorefining - Alexandria	60
(H) Middle Wabash – Little Vermillion	5,887	3,480	Valero Energy	100

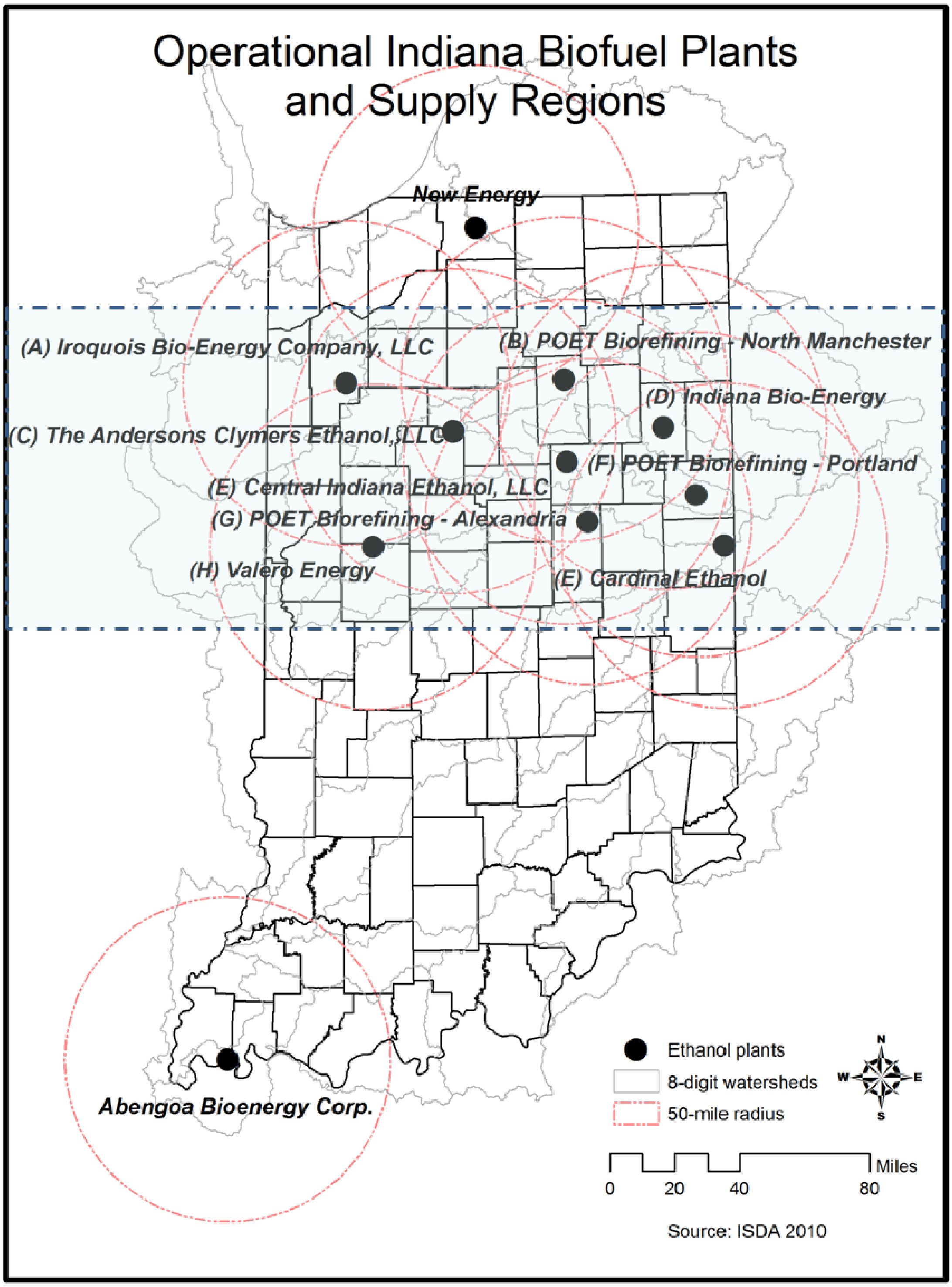

Figure 1. Corn-based ethanol plants in Indiana and the site selection for water use regime construction based on their relative distances. Blue highlighted area represents the geographic area within which the hydrogeologic characteristics are expected to be similar.

Primary Findings

Water-use regime plots were generated for all of the watersheds evaluated, and will be included in a research publication that is being currently prepared. Here, we present some representative plots for the Salamonie watershed (Figure 2) to illustrate the water-use regimes, and summarize the primary findings based on similar analyses in all other watersheds.

1. Given the humid climate and because crop irrigation is not a dominant demand, water regime plots at the *watershed scale* suggest minimum freshwater stress at the annual or even monthly time scales under *average* weather conditions. That is, consumptive uses of freshwater withdrawals by major sectors (utilities and industries) are small (even the maximum h_{out} is less than 0.1, which means no stress according to criticality ratio). Note that the data points lie on or close to the 1:1 line (withdrawals ~ return flows).
2. This evaluation, however, changes dramatically when *water-quality impairment* is accounted for in construction of the water-use regime plots; all watersheds we evaluated would be judged to be under severe water stress. Here, we considered water quality impairment from non-point sources. Stream concentrations of the herbicide atrazine exported from watersheds (based on % area planted to corn) was used to represent surface water quality impairment.
3. We have assumed that pollutant discharges from point sources (e.g., industrial operations, including biorefineries) meet all regulatory standards such that water quality is above acceptable thresholds for human and ecological health. However, further research is needed to establish that our assumption is indeed valid.
4. Under *drought conditions*, all watersheds we examined would be judged as being under severe stress both from quantity and quality perspectives. In case of Salamonie watershed, the water stress in summer season increased beyond 0.2 (mid-stress) and reached 0.45 (high-stress) in August.
5. Competing demands for freshwater are most likely to be experienced at spatial scales smaller than a watershed scale. That is, at a township or community level, freshwater demands from multiple sectors would be a significant issue as new demands from biorefineries are added. This is especially important since freshwater withdrawals are from groundwater sources, but return flows are to surface waters (streams). Thus, continued depletion by increasing pumping from aquifers can, over time, result in significant water stress at the local level.
6. Freshwater use data we utilized in our analysis came from USGS reports which are published once every five years and are available aggregated only at the county level. We did not access data that might be available with the local authorities who issue permits for groundwater use. Our assessments would be enhanced if such local-scale data were used to generate the water regime plots, and these plots would be even more useful to local water managers.
7. With likely changes in rainfall patterns [e.g., increasing probability of intense extreme events of floods and droughts], increasing competition for freshwater resources is expected. As such, careful assessment of shifting water-use regimes [increased stress] is needed in water allocation decisions.

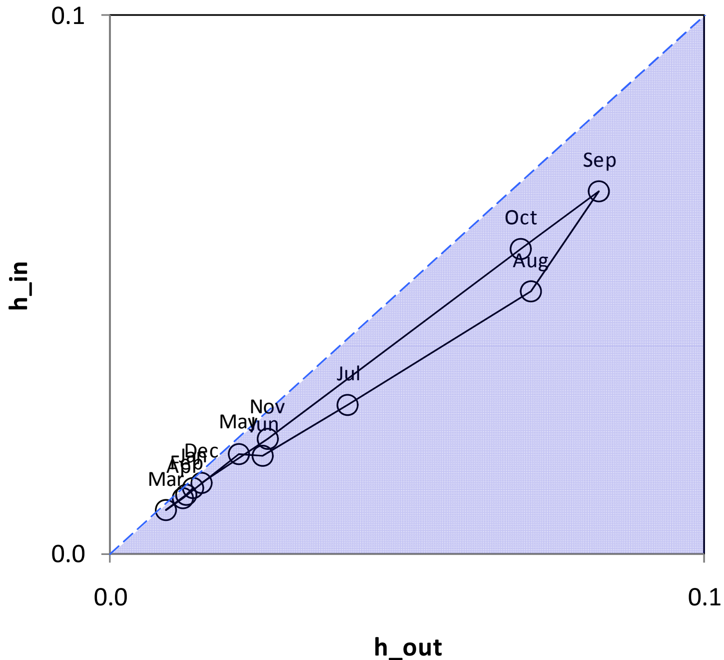

Figure 2A. Monthly variation of water use regime in mean weather condition <u>without the consideration of water quality.</u>

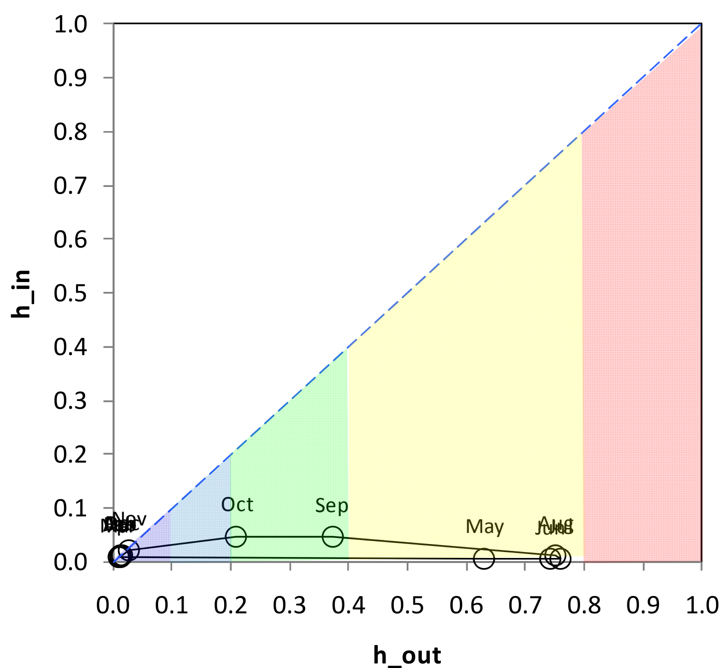

Figure 2B. Monthly variation of water use regime in mean weather condition <u>with the consideration of water quality</u>

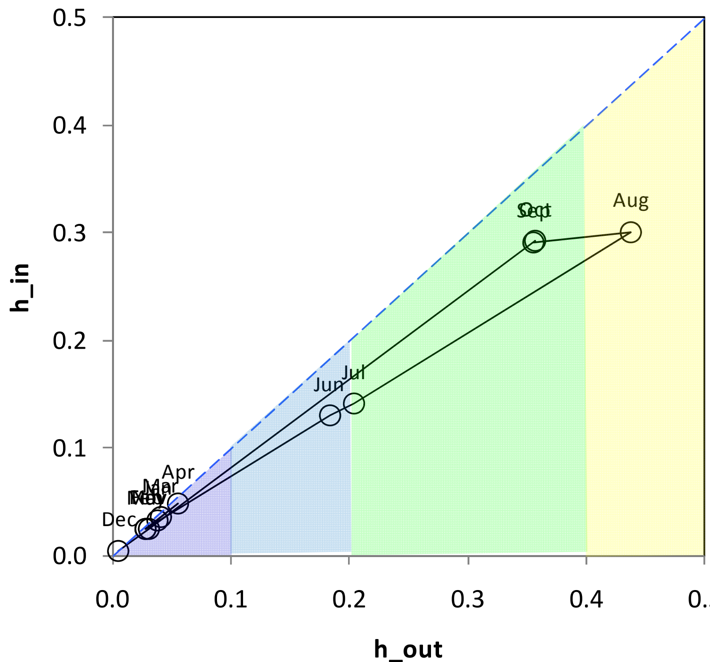

Figure 2C. Monthly variation of water use regime under extreme drought condition without the consideration of water quality

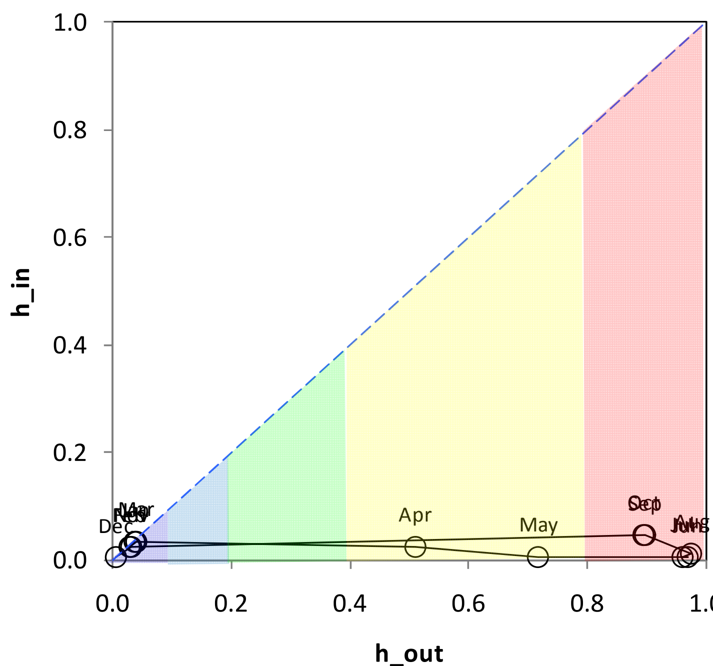

Figure 2D. Monthly variation of water use regime under extreme drought condition with the consideration of water quality

Practical Implications

Current water-use status of biofuel refineries located in several watersheds within central Indiana was evaluated. Our results will provide an assessment tool as well as critical information to local governments and water management authorities to: (1) assist successful decision making on selecting which biomass conversion technology should be adopted, (2) where to locate these technologies in terms of minimizing local and regional impact on fresh water resources; and (3) plan sustainable expansion of biofuel production to reach overarching goals of energy independence.

Graduate Student training

This project was lead by Mr. Jeryang Park (CE PhD), mentored by Professor Suresh Rao (CE). Mr. Parks' PhD dissertation topic focuses on modeling resilience of biofuel production systems, and the dynamics of coupled industrial systems (biorefineries) and natural systems (biomass production; water resources). His research will examine adaptive strategies needed to promote sustainability of biofuel production under volatile (i.e., stochastic forcing & feedbacks) of climate and markets. Mr. Park assisted Professor Rao in teaching the Global Water Resources Sustainability (CE597), a graduate course taught during spring 2010 semester. This inter-disciplinary course had an enrollment of about 15 graduate students, derived from engineering, agriculture, and liberal arts programs. The class included several students from the Ecological Science and Engineering Inter-disciplinary Graduate Program (ESE-IGP). Initial parts of this study (e.g., data gathering; conceptual model development, etc) were conducted as a class project within this CE597 course. Mr. Park led a group of the following students to compile the data, and develop the preliminary assessment: Carson Reeling (M.S. student; Agricultural Economics Department); Elizabeth Cox (M.S. student; ESE-IGP); Ryan Hultgren (senior; Civil Engineering), Kasey Faust (M.S. student; Civil Engineering). Mr. Reeling played a key role throughout the project period in working with Mr. Park and Dr. Rao to compile the data, complete the data analyses, and generate the final report.

Graduate Student Evaluation [Carson Reeling]

In the spring of 2010, I enrolled in Dr. Rao's class, "Water Resources and Sustainability." My training is in agricultural economics, but having been born and raised in the high desert of Eastern California, I am particularly interested in water resource management. I was therefore very happy to find a class in water resource management that, despite being taught in the civil engineering department, was highly accessible to students of different backgrounds.

A requirement of the class was to develop a term project that explored some component of water resource sustainability. Dr. Rao and his graduate student, Jeryang Park, presented me and other classmates with the opportunity to satisfy this requirement by contributing to the research project supported by your grant. I believed that the project had the potential to be both challenging and successful, so I chose to participate.

Having worked on the project over the course of spring semester, my initial assessment proved to be correct. The project challenged me to expand my academic horizon beyond economics and into the physical sciences. While previously only economic considerations seemed relevant, analyzing the basic hydrology behind biofuel plant location decisions and the effects of agricultural production on water quality taught me the value of expanding my perspective to take a more systems-oriented approach to researching environmental issues.

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A First Assessment of Pharmaceuticals and Personal Care Products in the Middle Wabash River, Indiana

Basic Information

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End Date:	2/28/2011
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Congressional District:	4
Research Category:	Biological Sciences
Focus Category:	Agriculture, Ecology, Education
Descriptors:	
Principal Investigators:	Marisol Sepulveda

Publications

There are no publications.

Title: A First Assessment of Pharmaceuticals and Personal Care Products in the Middle Wabash River, Indiana

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Abstract: Measureable quantities of numerous pharmaceuticals and personal care products (PPCPs) have been found downstream of sewage wastewater treatment plants (SWWTP) and animal farms across the U.S. Because they were synthesized to combat specific human diseases, they tend to target specific tissues at very low doses. At the parts-per-billion and parts-per-trillion levels, they can affect reproduction, embryo development, and behavior of fish and other aquatic organisms. The Wabash River is one of the largest rivers in the Midwestern U.S. and of great ecological and economical importance. Despite the clear evidence of the potential impact of PPCPs to aquatic communities and their likely presence in the Wabash River watershed, no data is currently available on these chemicals in this region. Our objectives were to: (1) quantify water concentrations of environmentally relevant PPCPs in two Middle Wabash River sites that represent different degrees of SWWTP effluent contamination as well as from the West Lafayette SWWTP (influent and effluent); and (2) educate local communities about the human and ecological health implications of our findings. Using Enzyme-Linked Immunosorbent Assays (ELISAs) we quantified concentrations of an antibiotic (Tylosin), an antimicrobial (Triclosan), and a synthetic estrogen (ethinylestradiol, EE_2). Tylosin was found ubiquitously in all sites (mean ± standard deviation for all sites combined was 2.52 ± 1.5 µg/L, range of 0.05 – 6.1 µg/L). Effluent concentrations were lower than influent ones (1.26 vs. 2.82 µg/L) which suggests biodegradation of this chemical within the SWWTP. In contrast, Triclosan and EE_2 were only found in SWWTP samples. Triclosan was detected only in influent samples at a concentration of 1.47 ± 0.41 µg/L (0.99 – 2.24 µg/L). EE_2 was only detected in three occasions: twice in the influent (0.06 and 0.07 µg/L) and once in the effluent (0.058 µg/L). With exception of EE_2, all concentrations are below those reported to negatively impact aquatic life. It is important to note that once the effluent reaches the Wabash River, EE_2 concentrations will be diluted down significantly. Very little information exists on the effects of Triclosan and Tylosin on aquatic organisms and more studies are needed in order to determine safe levels. Follow-up studies that verify these values using standard mass spectrometry techniques as well as quantify other types of PPCPs and their potential effects are needed.

In an effort to convey these results to the public while increasing their awareness toward PPCPs and their effects on the environment, an outreach program was created. This effort included development of a website (www.wabashriver.net/pharmaceuticals), quarterly press release distribution, and a public meeting. Individual interest in PPCPs and their fate in the environment are high within Greater Lafayette. This is evidenced by the 22 website hits per month throughout the length of the project and the 24 people who attended the final public meeting.

Problem: Pharmaceuticals and personal care products (PPCPs) are a new class of emerging contaminants. These compounds include antibiotics, antimicrobials, fungicides, cholesterol-lowering drugs, beta-blockers, anti-inflammatory drugs, anti-epileptic drugs, anti-depressants, hormones, and fragrances. Discharges of sewage wastewater treatment plants (SWWTPs) and runoff from crops land-applied with animal wastes are the main sources of these chemicals to the environment. Although each compound is ingested at small concentrations, the population as a whole consumes large quantities. Many of these compounds pass unaltered into feces and urine and end up in the sewage treatment process. In addition, many unused pharmaceuticals are disposed of directly through the sewage system. Pharmaceuticals are also structurally stable and can cross lipid layers, bio-accumulating in fish (Brooks et al. 2005; Ramirez et al. 2009). Despite the large potential for PPCPs to impact aquatic ecosystems, relatively little research has been conducted to date to assess the environmental effects of these chemicals.

PPCPs are different from conventional contaminants in many respects. Because they are synthesized to combat specific human diseases after years of pharmaceutical research, they tend to target specific tissues and physiological functions that are well conserved across all vertebrates. This, in turn, translates into a high potency, which is supported by the fact that recent laboratory studies have shown effects in non-target organisms at very low concentrations (i.e., sub-parts-per-billion and parts-per-trillion levels). The bulk of these studies relate to effects of a synthetic estrogen used for birth control, ethynil estradiol (EE_2), which was reported to cause ova-testis in fish over a decade ago. In addition, non-steroidal anti-inflammatory drugs and anti-depressants can cause reproductive problems in fish and crustaceans (Gagne and Blaise 2003; Pascoe et al. 2003; Foran et al. 2004), and fluoxetine, the active ingredient of Prozac, has been shown to alter social (Perreault et al. 2003) and predatory (Semsar et al. 2004) behaviors as well as osmoregulation (Morando et al. 2009) in fish. However, the effects of most other PPCPs remain largely unknown at this time.

The Wabash River is one of the largest rivers in the Midwestern U.S., extending for close to 800 km from Northeastern Indiana at the Ohio border to Southwest Indiana where it merges with the Ohio River. Over its course it crosses five 8-digit Hydrologic Units (HUC) and 19 counties. Approximately, one third of Indiana’s population lives within one of these 19 counties. The Wabash River and its tributaries provide drinking water as well as great economic (agriculture, energy production) and recreational (fishing, swimming, canoeing) opportunities. In addition, the Wabash River drainage is considered one of the richest river segments in the nation being home for over 100 species of plants and animals that are considered endangered, threatened, or rare.

Despite the clear evidence of the potential impact of PPCPs to aquatic communities and their likely presence in the Wabash River watershed, no data are currently available on these chemicals in this region. We propose to conduct a first assessment of a representative group of PPCPs in this region to determine their concentration in water. We will also help inform the public about our findings and the issue of PPCPs in the environment in general through the activities of a local non-profit organization centered on Wabash River conservation.

Research Objectives: (1) Quantify water concentrations of a range of environmentally relevant PPCPs in three Middle Wabash River sites that represent different degrees of WWTP effluent contamination; and (2) Educate local communities about the human and ecological health implications of our findings. Originally we listed an additional objective, which was to quantify the concentration of 1 or 2 PPCPs in fish fillet. Because concentrations detected in water (see below) were very low, we decided not to measure them in fish tissues. In addition, we could not find a fish species that was present in all three sites for comparison purposes.

Methodology: Study sites - We selected the following sites for our study: 1) Little Pine Creek; 2) Little Wea Creek; and 3) the West Lafayette SWWTP (see red circles in **Fig. 1**). The SWWTP was selected as a "worse-case" scenario in terms of PPCPs in water. The Little Pine and Little Wea Creek subwatersheds are tributaries that flow into the Wabash in the vicinity of Lafayette and West Lafayette. The Little Pine Creek site flows through agricultural lands, but it does not receive SWWTP and is being used as a non-managed reference site in a related Section 319 Nonpoint Source funded watershed management plan project. The Little Wea Creek site is surrounded by agricultural land, receives no SWWTP effluents, but will be subject to management activities in the developing 319 watershed management project referenced above. In addition, co-PI Reuben Goforth is conducting fish monitoring efforts at both of these sites, sampling fish communities four times/yr. Thus in the near future, we will have the opportunity to potentially assess the relationship between PPCPs levels and fish community parameters. Finally, co-PI Sara Peel from the Wabash River Enhancement Corporation (WREC), is working with local communities from these watersheds to help them develop management plans for these tributaries, and her ongoing involvement with people living on these watersheds will thus allow for an easier communication of our results and potential inclusion of these data in their management plans.

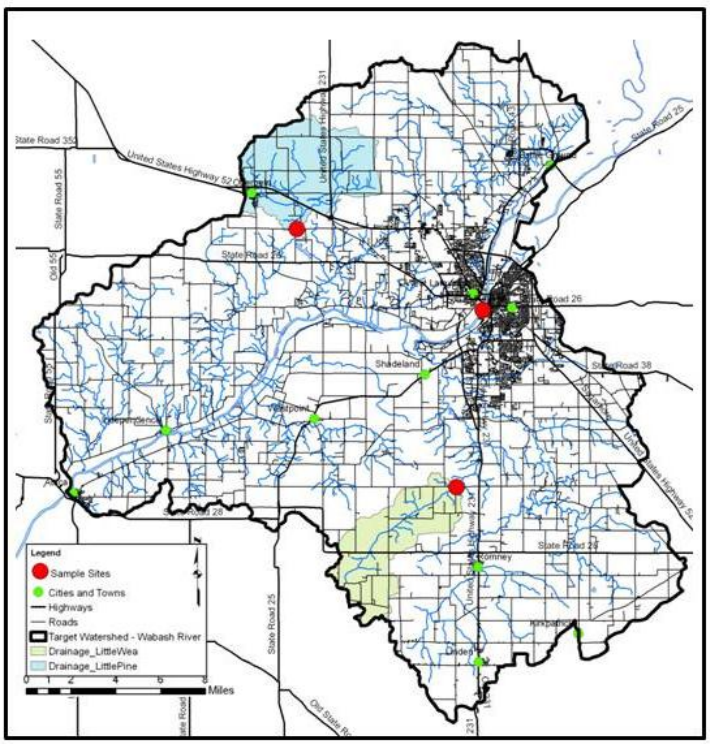

Figure 1. Map of the upper Wabash watershed showing the sampling locations (red circles).

Sampling and analytical methods. - Gas chromatography–mass spectrometry (GC-MS), high performance liquid chromatography (HPLC), and LC-MS are considered the "standard" methods for quantifying PPCPs. However, immunoassay techniques, particularly ELISAs, have become increasingly popular for measuring these and other contaminants due to their high sensitivity, ease of use, short analysis time, and cost-effectiveness. Indeed, several recent studies measuring PPCPs have reported high concordance between traditional methods and ELISAs (Aga et al. 2003; Deng et al. 2003; Huoa et al. 2007; Brun et al. 2008; Dolliver et al. 2008). Immunoassay analytical detection is based on the capability of antibodies to specifically recognize and form stable complexes with antigens. Immunoassays employ antibodies as analytical reagents. In ELISA test kits, an enzyme conjugate competes with the chemical in the sample for a limited number of binding sites on the antibody coated plate or particle. The extent of color development is inversely proportional to the amount of chemical in the sample and is quantified using a plate reader.

Water samples (1 ml or 25 ml, see below) were collected every other week from April 2010 to March 2011. All sample bottles were amber glass to prevent photo-degradation of the analytes. Immediately after collection, samples were taken to the laboratory in coolers (~4°C) and immediately prepared (see below) and extracts frozen (-20°C) until analyzed.

Sample preparation varied depending on the chemical. For EE_2, samples were allowed to thaw (~4°C) and then two samples combined for 50 ml monthly samples. Samples were filtered (1 µm glass fiber, ADVANTEC Co., Shanghai, China) and the filtrate concentrated to 1 ml using SPE cartridges (Strata SDB-L Styrene-Divinylbenzene Polymer, 100 µm, Phenomenex, Inc., Torrance, CA, USA). Cartridges were then washed with distilled water, allowed to dry by applying vacuum for 1 min, and washed with hexane. The extract was then transferred to methanol (10%) and the solvent evaporated with nitrogen gas. For Triclosan, water samples were diluted to 25% methanol and frozen upon collection, and for Tylosin, samples were diluted 1:10 (stabilizer:sample) and frozen as 1 ml samples upon collection.

All ELISAs (Abraxis®) were 96-microtiter plate assays and were run following manufacturer's instructions (more information about these kits can be found by following these links EE2, Tylosin, Triclosan). Briefly, samples and standards were added to the microwells followed by specific antibodies against the PPCP of interest. The mixture was then be incubated and wells washed before addition of the peroxidase conjugated secondary antibody. This was followed by a second incubation and wash. Finally, substrate (urea peroxide) and chromogen were added to each well and absorbances measured at 450 nm using a Dynex Technologies MRX Revelation microplate reader.

Outreach activities – The Wabash River Enhancement Corporation (WREC) created an education and outreach program using web and news media outreach and a pharmacy outreach program. This web site was created as a link to WREC's website, while media contacts were generated from WREC's contact list. The pharmacy outreach program contact list was generated from online resources as well as web and paper directories for the region.

Results: Tylosin was found ubiquitously in all sites (**Table 1**). Mean concentration (± standard deviation) for all sites combined was 2.5 ± 1.5 µg/L (range of 0.05 – 6.1 µg/L). Effluent concentrations were lower than influent samples (1.26 vs. 2.82 µg/L) which suggests biodegradation of this chemical within the SWWTP. Tylosin concentrations were below those reported to negatively impact aquatic life (but see below since not a lot of information is available on the impacts of this chemical). In contrast, Triclosan and EE_2 were only found in SWWTP samples (**Tables 2 and 3**). Triclosan was detected only in influent samples at a concentration of 1.47 ± 0.41 µg/L (0.99 – 2.24 µg/L), thus there was a significant reduction (to non-detectable levels) of this bactericidal within the SWWTTP. EE_2 was only detected in three occasions: twice in the influent (0.06 and 0.07 µg/L) and once in the effluent (0.058 µg/L). It is important to note that once the effluent reaches the Wabash River, EE_2 concentrations will be diluted down significantly and very likely reach non-detectable levels.

Very little information exists on the effects of Triclosan and Tylosin on aquatic organisms and more studies are needed in order to determine safe levels. Lowest Observable Effect Concentrations (LOEC) measured as inhibition of growth in algae has been reported at 0.40 and 64 µg/L for Triclosan and Tylosin, respectively (Yang et al. 2008). In frogs, exposure to Triclosan (0.15 – 22 µg/L) resulted in disruption in the expression of thyroid-hormone associated genes as well as in increased growth rates (Veldhoen et al. 2006). Thus, although Triclosan concentrations from the influent SWWTP fell within ranges reported to cause inhibition of algae growth and alterations in amphibian development, no detectable levels of this pharmaceutical were detected in the effluent meaning no significant amounts were being released to the Wabash River. Follow-up studies that verify these values using standard mass spectrometry techniques as well as quantify other types of PPCPs and their potential effects are needed.

The WREC led several education and outreach activities through this project. The main components of the outreach program focused on provision of information to the public and encouragement to use available and up-coming drug drop-off programs. WREC established a website (www.wabashriver.net/pharmaceuticals) to provide information about this project, environmental impacts of PPCPs, PPCP information for the region and state, and local and statewide drug drop-off information. Secondarily, WREC established a press and pharmacy outreach program. Quarterly (4) press releases were sent to regional radio, television, and newspaper contacts to establish lines of communication for this effort. Two newspaper (Lafayette J & C) articles were written about this study and its findings http://www.jconline.com/article/20110327/NEWS02/103270340/Program-focuses-study-drugs-Wabash and http://www.jconline.com/article/20110330/NEWS/103300321/Discarded-drugs-do-reach-Wabash?odyssey=tab|topnews|text|FRONTPAGE.

The local television channel 18, also aired a small note about the issue of PPCPs in the environment. The pharmacy outreach program resulted in the compilation of all pharmacy, veterinarian, and long-term care centers contacts with all contacts being invited to participate in the final meeting to discuss results of the study and review options and programs related to proper PPCP disposal.

Table 1. Summary of Tylosin data (µg/L) collected during this project. Note that creek samples were collected at different times compared to SWTTP samples. Two water samples were pooled for each analysis. ND = Not Detected.

Date of Collection (2010-2011)	West Lafayette SWWTP Influent	Effluent	Little Pine Creek	Little Wea Creek
4/9 & 4/23 **4/1 & 4/16**	4.17	1.96	 3.20	 2.53
5/7 & 5/21 **5/13 & 5/25**	0.49	2.23	 0.89	 6.13
6/4 & 6/24 **6/24 & 7/8**	 3.65	 0.61	 3.28	 5.86
7/9 & 7/16	ND	1.00		
7/30 & 8/13 **7/22 & 8/3**	2.94	0.05	 1.00	 3.17
8/27 & 9/10*	0.55	2.71	4.48	4.34
9/23 & 10/8 **9/15 & 10/1**	4.48	0.56	 2.25	 2.56
10/23 & 11/5 **10/14 & 10/28**	2.42	1.40	 2.14	 2.01
11/15 & 11/24			1.11	1.58
12/10 & 12/21			3.74	0.93
2/26 & 3/2	3.89	0.77	ND	2.97
Mean ± SD	2.82 ± 1.57	1.26 ± 0.88	2.45 ± 1.29	3.21 ± 1.73

*Actual collection date for Little Wea and Little Pine Creeks was 9/3/2010.

Table 2. Summary of Triclosan data (µg/L) collected during this project. Triclosan was not detected in any of the creek samples nor the SWTTP effluent samples. Two water samples were pooled for each analysis.

Date of Collection (2010-2011)	West Lafayette SWWTP Influent
4/9 & 4/23	2.24
5/7 & 5/21	1.28
6/4 & 6/24	1.17
7/9 & 7/16	0.99
7/30 & 8/13	0.85
8/27 & 9/10	1.85
9/23 & 10/8	1.37
10/23 & 11/5	1.83
11/19 & 12/3	1.30
2/26 & 3/2	1.63
Mean ± SD	1.47 ± 0.41

Table 3. Summary of ethinyl estradiol (EE_2) data (µg/L) collected during this project. EE_2 was only detected in SWWTP samples. Two water samples were pooled for each analysis. ND = Not Detected.

Date of Collection (2010-2011)	West Lafayette SWWTP Influent	Effluent
4/9 & 4/23	0.060	ND
5/7 & 5/21	ND	0.058
6/4 & 6/24	0.074	ND
7/9 & 7/16	ND	ND
7/30 & 8/13	ND	ND
8/27 & 9/10	ND	ND
9/23 & 10/8	ND	ND
10/23 & 11/5	ND	ND
11/19 & 12/3	ND	ND
2/26 & 3/2	ND	ND
Mean ± SD	0.068 ± 0.008	-

Major Conclusions and Significance: Overall, the concentration of PPCPs detected from the different areas sampled was low and fell below threshold values known to impact aquatic biota. However, it must be kept in mind that little information exists on the impacts of Tylosin and Triclosan on aquatic organisms. Results from this study benefited the state of Indiana by: 1) Providing data on PPCPs in the environment which could be used to prioritize which compounds may be of greatest threat to both aquatic communities and human health and in need of monitoring and regulation; and 2) Informing the public about the issue of PPCPs in the environment and ways to decrease their release to the environment.

Presentations and Websites: The PPCP website received high interest from the community with an average of 22 hits per month during the project period. This website will continue to serve as a source of information for future PPCP efforts and drug drop-off programs and opportunities. The public meeting generated some interest and subsequent public events continue to reference this effort to quantify PPCP impacts to the Wabash River. The pharmacy outreach program expanded from its original intent to cover long-term care and veterinary facilities as well. Responses to this program were modest possibly based on efforts already in place at the state level targeting correct PPCP disposal on the commercial end. Efforts focusing on maintaining permanent drop med locations and drug disposal programs of easy access are needed.

Grant Submissions: No grants have been submitted yet.

Students/Technical Staff: Megan Heller (Ph.D student working under the supervision of Dr. Ron Turco) participated by collecting all water samples from the creeks. Guy Telesnicki and Jennifer Meyer (technical staff from the Department of Forestry and Natural Resources) collected all samples from the SWWTP and run the ELISAs.

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Transport, Fate, and Effects of Pharmaceuticals derived from Animal Feeding Operations: A comprehensive assessment of central Indiana streams

Basic Information

Title:	Transport, Fate, and Effects of Pharmaceuticals derived from Animal Feeding Operations: A comprehensive assessment of central Indiana streams
Project Number:	2010IN243B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	6
Research Category:	Water Quality
Focus Category:	Agriculture, Ecology, Hydrology
Descriptors:	
Principal Investigators:	Melody J. Bernot

Publications

There are no publications.

Local and Regional Impacts of Biofuel Production Facilities on Freshwater Quantity and Quality in Indiana

Report as of FY2010 for 2010IN219B

Publications

Project 2010IN219B has resulted in no reported publications as of FY2010.

Report Follows

IWRRC 2010 Project Report

State: IN **Project Number:** 2010IN219B
Title: Local and Regional Impacts of Biofuel Production Facilities on Freshwater Quality in Indiana
Project Type: Research
Focus Category: MOD, WQL, WQN, WU
Keywords: Freshwater availability; blue and green water; water use; biofuel; water quality
Start Date: 3/01/2010 **End Date:** 2/28/2011
Congressional District: 4 **PI:** P. Suresh C. Rao **email**:pscr@purdue.edu

Abstract / Summary
Freshwater plays a crucial role in all stages of biofuel production - from biomass cultivation through its conversion into biofuel. Corn ethanol production increases may further compromise water quality and compete with other sectors of freshwater use (e.g., urban and industrial). The effects of expanded biofuel production on freshwater, a limited but a renewable natural resource, need to be considered as demand for freshwater from various sectors increases and places additional stress on already constrained freshwater supplies. An increase in corn cultivation using current intensive agricultural practices will also impair water quality as a result of the runoff of fertilizer and pesticides into surface water and groundwater. Moreover, biorefineries also discharge wastewater containing several inorganic and organic contaminants that could impair surface-water quality and compound the problem on already impaired freshwater. Therefore, both quantity and quality of freshwater should be considered when assessing the impacts of biofuels production expansion on local and regional freshwater. The water use regime, originally proposed by Weiskel et al. (2007), is adopted for this research and modified to take into account water quality impacts by non-point sources in addition to quantity on the degree of human influence on region's hydrology. The *criticality ratio* is also combined as a method of determining water stress. Eight watersheds (HUC-8), within which biorefineries are currently in operation and are located within the band of mid-northern part of Indiana, were selected for an evaluation of shifts in "water-use regimes". Our analysis shows that, at the *watershed scale,* the consumptive water uses from various major sectors are small under average weather conditions. This evaluation, however, changes dramatically when *water-quality impairments* are taken into account; all watersheds we evaluated would be judged to be under severe water stress. Moreover, under *drought conditions*, all watersheds we examined would be judged to be under severe stress both from quantity and quality perspectives. Competing demands for freshwater are most likely to be experienced at spatial scales smaller than a watershed scale. This is especially important since freshwater withdrawals are from groundwater sources, but return flows are to surface water (streams). Thus, continued depletion by increasing pumping from aquifers can, over time, result in significant water stress conditions. Freshwater use data we utilized in our analysis came from the USGS reports which are published once every five years, and are available aggregated only at the county level. We did not access data that might be available with the local authorities who issue permits for groundwater use. Our assessments would be enhanced if such local-scale data were used to generate the water regime plots, and these plots would be even more useful to local water managers. Hydro-climatic shifts projected climate change [increased frequency of extreme events] would increase the likelihood of water-stress in the watersheds.

Statement of Critical Regional/State Freshwater Problem

The annual bioethanol production capacity in the United States has increased rapidly and reached 55 billion liters as of January 2009. Indiana, a major contributor to this trend, is the sixth highest bioethanol producing state (RFA 2010). Water plays a crucial role in all stages of biofuel production - from cultivation of feedstock through its conversion into biofuel (Aden 2007). The National Research Council (Hill et al. 2006) and other studies (Donner and Kucharik 2008) have warned that the corn ethanol production increases may further compromise water quality and compete with other sectors of water use (e.g., urban and industrial).

Freshwater is a limited, but a renewable natural resource, and many parts of the world or even the United States are already experiencing water scarcities. These scarcities are complicated by increasing demands of a growing population and economies. Moreover, as demand for water from various sectors increases and places additional stress on already constrained freshwater supplies, the effects of expanded biofuel production may need to be considered (GAO 2009). Although, total surface water withdrawals for Indiana did not show significant increasing trend over time, relatively large annual fluctuations have occurred (Indiana State 2008). Moreover, it is important to take into account the local or regional variability of water availability and also current and projected use trends. According to GAO's 2003 survey, Indiana was among the states which, under average water conditions, that are likely to experience water shortages in one or more localized areas within 10 years from the surveyed year (GAO 2003). Some communities have become concerned that freshwater withdrawals for biofuels production would have adverse impacts on their drinking water and municipal supplies, and are pressuring states to limit water use by bioethanol facilities. For example, at least one Minnesota local water district denied a permit for a proposed biorefinery based on concerns about limited water supply in the area (GAO 2009).

An increase in corn cultivation using current agricultural practices will also impair water quality as a result of the runoff of fertilizer and pesticides into surface water and groundwater, leading to impacts at the scales of the entire Mississippi River Basin and the Gulf of Mexico (e.g., Donner et al. (2004) and Donner and Kucharik (2008)). Fertilizer runoff can lead to nutrient enrichment, harmful algal blooms, decreased water clarity, and anoxia in the water, all of which impair aquatic habitats. The application rates of atrazine, a commonly used herbicide for corn production, are highest in the Corn Belt, and it was also the most widely detected pesticide in watersheds in this area (Capel and Larson 2001). Moreover, biorefineries also discharge wastewater containing several inorganic and organic contaminants that could impair surface water quality (Schnoor et al. 2008). However, the type of contaminants discharged varies by the type of biofuels produced and the biomass conversion technology used. For example, ethanol biorefineries generally discharge chemicals or salts that build up in cooling towers and boilers or are produced as waste by reverse osmosis, a process used to remove salts and other contaminants from water prior to discharge from the biorefinery. In contrast, biodiesel refineries discharge other pollutants such as glycerin that may be harmful to water quality (GAO 2009).

According to Indiana Department of Environmental Management (IDEM), Indiana's water bodies have already been highly impaired in terms of organic compounds (rank 1 among U.S. states) and biological community (rank 7), and that this situation is likely to only increase (Indiana State 2010). Although, there is multitude of sources for freshwater contamination, the increase of biofuels production will compound the problem because biorefineries produce wastewater with high concentration of organic and inorganic constituents and they require high amount of freshwater use. New source of freshwater (most likely, groundwater) is required to treat or dilute the contaminated effluents from biofuels production process. Therefore, both quantity and quality of freshwater should be considered when assessing the impacts of biofuels production expansion on local and regional freshwater.

Related Research

There have been several efforts to estimate water use for biofuel production. Gerbens-Leenes et al. (2009) estimated the water footprint (WF) of bioenergy from 12 crops that currently contribute the most to global agriculture production. Although, they had calculated the WF of each crop by country and bioenergy to be produced, this study is focused only on the agricultural (biomass) production stage. To overcome the limitations of prior studies, which had not accounted for the varied regional irrigation practices on estimating the water requirement for bio-ethanol production, Chiu et al. (2009) used regional time-series data for agricultural and ethanol production in the U.S. to estimate state-level field-to-pump water requirement of bioethanol across the nation. They estimated the embodied water in ethanol by state and evaluated the local impacts in terms of groundwater withdrawal caused by bio-ethanol production; however, they only considered the corn ethanol industry even when projecting the expansion of the biofuels industry.

Data Analysis & Technical Approach

Since most of the studies have been done at a large scale, global or national, and are highly focused on feedstock growth, this study aims to investigate local and regional impacts of freshwater use and wastewater discharges, especially from biofuel conversion processes. Indiana, in USDA farming Region 5, does not use much irrigation water for feedstock cultivation compared to other Regions, which means changing or increasing feedstocks production will not have much impact on freshwater withdrawals. Therefore, freshwater uses in biorefineries for biomass conversion will have relatively high potential to introduce local- or regional-scale conflicts for competing uses and quality impairment. Thus, water required for biomass conversion facilities will especially be highlighted in this research. While freshwater uses for biofuels conversion processes have local impacts on water problems, the discharge of wastewater effluents from those facilities have potential to expand the scale of the problem to region or interstate levels. However, wastewater quality from biorefineries has not been investigated.

The methods used to determine the appropriateness of bioethanol plant locations in Indiana follow those outlined by Weiskel et al. (2007). The method is briefly explained below, and the reader is referred to Weiskel et al. (2007) for more detailed explanation. In this study, a water-use regime is created for each watershed containing a bioethanol plant. The water use regime is defined by considering the water balance of a bounded watershed.

$$P + (GW_{in} + SW_{in}) + H_{in} - \Delta S/\Delta t = ET + (GW_{out} + SW_{out}) + H_{out} \qquad (1)$$

where P is precipitation; $(GW_{in} + SW_{in})$ is groundwater and surface water inflows; ET is evapotranspiration; $GW_{out} + SW_{out}$ is groundwater and surface water outflows; H_{in} is total return flow to the control volume from all sources, including return flows from local withdrawals and imported withdrawals; H_{out} is withdrawals from the control volume; and $\Delta S/\Delta t$ is the rate of change in control volume storage (surface and subsurface). All units are volume/time (L^3/T).

Although, Weiskel et al. (2007) recommended consideration of stream basins and aquifers separately, it is assumed here that the change of net storage in aquifer is negligible when averaged over the period of interest, which implies $GW_{in} \approx GW_{out}$. Thus, overall water balance is mainly determined by the change of surface water flow. This assumption is feasible because, in Indiana, most of the water demand in agricultural sector, which generally is the major source for local freshwater demand, is known to be fulfilled by rainfall and the irrigation rate from groundwater is relatively low (Wu et al. 2009). Therefore, only the water balance for stream basin is explicitly evaluated for this study. In this case, the total water balance can be rewritten as:

$$P + SW_{in} + H_{in} - \Delta S/\Delta t = ET + SW_{out} + H_{out} \tag{2}$$

The net basin flux (NetFlux), which may be directly available for human use can be derived by rearranging the Eq. (2).

$$\begin{aligned} NetFlux &= (P - ET) + SW_{in} + H_{in} - \Delta S/\Delta t \\ &= SW_{out} + H_{out} \end{aligned} \tag{3}$$

According to Eq. (3), two different forms can be used to obtain net flux depending on the data available. When the latter form of net flux is used, only two data sets, outflow of surface water and human water withdrawal, are required and those are typically available.

When considering water quality issues, the quantity that is hypothetically imported into the closed basin (W_{dilute}) to dilute the contaminated surface water should be added to the net flux. Thus, the latter form of Eq. (3) is rewritten as:

$$NetFlux = SW_{out} + H_{out} + W_{dilute} \tag{4}$$

All terms in the water balance are normalized by dividing each term by the net system flux, which yields normalized human inflow (h_{in}) and outflow (h_{out}). Eq. (3) is used for estimating h_{in} and h_{out} without considering the water quality issue, while Eq. (4) is used when water quality is considered.

$$h_{in} = H_{in}/NetFlux \tag{5}$$

$$h_{out} = H_{out}/NetFlux \tag{6}$$

Plotting h_{in} versus h_{out} [calculated by Eq. (5) and (6)] for each watershed yields the water use regime. The target for water use intensity is a one-to-one ratio of h_{in} to h_{out}, or the 45° line that is seen on the graphs shown in the Result section. This line represents a state in which imports = exports, although the water returned is not necessarily of the same quality as the water withdrawn. In the water regime plots, the region below the 1:1 diagonal line represents the "withdrawal regime" (i.e., withdrawals > imports), and the region below the diagonal represents the "import regime" (imports > withdrawals). Unsustainable freshwater withdrawals may arise either from large withdrawals or significant water quality impairment or both.

The derivation of the freshwater-use regime is useful for analyzing the intra-seasonal and geographic differences within and among watersheds. However, the water-use regimes demonstrate the degree of human influence on a region's hydrology and not necessarily the water stress that results from such a condition. An objective measure must be derived to assess the relative water stress implied by a given watershed's water use regime. The criticality ratio – defined by Alcamo et al. (2000) as the ratio of water use to water availability – is used as a method of determining water stress. The levels of water stress are defined below:

- 0 – 0.1: no stress
- 0.1 – 0.2: low stress
- 0.2 – 0.4: mid stress
- 0.4 – 0.8: high stress
- 0.8 – 1: very high stress

These criticality ratios can be directly applied to the water use regime. In the modified water use regime described above,

$$h_{out} = \frac{H_{out}}{NetFlux} \tag{7}$$

The criticality ratio is defined as:

$$\frac{water\ use}{water\ availability} = \frac{H_{out}}{(P-ET)+SW_{in}+H_{in}-\Delta S/\Delta t} = \frac{H_{out}}{NetFlux} = h_{out} \tag{8}$$

The above levels of water stressed defined by the criticality ratio can easily be included in the water use regime.

After deriving the water-use regime for each watershed, a worst-case scenario was examined to explore issues that may result in the inappropriateness of a certain location for ethanol production. Returning to the USGS stream flow measurement data, the discharge rate at the lower fifth percentile of all years was used in place of the mean discharge rate to re-calculate the water use regime. This reveals the main problem inherent with drought years: a much greater amount of water input is required to dilute harmful chemicals to acceptable levels. The water-use regimes were re-calculated using the twenty-fifth percentile of discharge data to demonstrate the effects of less extreme drought years.

Indiana Watersheds Evaluated

The freshwater use regime is constructed for the HUC-8 watersheds in which bioethanol plants are in operation to compare how freshwater use by biofuels production impacts local hydrologic stress. As of December 2010, Indiana had 12 completed ethanol plants and one more under construction (Figure 1). The combined ethanol production of the plants completed and the additional one under construction will exceed 1.1 billion gallons per year, which represents 7% of the U.S. ethanol industry (ISDA 2010). The biorefineries are located close to each other, and therefore conflicts over water use are likely to occur. Corn-based ethanol production with the nameplate capacities of 150 to 415 million liters typically requires feedstocks to be supplied from regions that stretch several tens of miles of radius from a plant's location. While production process itself may induce local conflicts over freshwater use, the spatial range of impact caused by feedstock production can be expanded far beyond the scale of county and even of a watershed. Thus, among the Indiana biorefineries, nine located in eight watersheds within a similar hydro-geologic region were selected (Table 1).

Table 1. Selected watersheds for the construction of water use regime.

Watershed	Total Area (km^2)	Crop (Corn) Area (km^2)	Biorefinery	Production Capacity (MG/year)
(A) Iroquois	2,208	902	Iroquois Bio-energy	40
(B) Eel (Upper)	2,112	1,313	POET Biorefining – North Manchester	65
(C) Middle Wabash Deer	1,731	1,259	The Andersons	110
(D) Upper Wabash	4,229	922	Indiana Bio-Energy	110
(E) Mississinewa	2,114	577	Central Indiana Cardinal Energy	40 100
(F) Salamonie	1,450	1,037	POET Biorefining - Portland	65
(G) Upper White	7,044	1,506	POET Biorefining - Alexandria	60
(H) Middle Wabash – Little Vermillion	5,887	3,480	Valero Energy	100

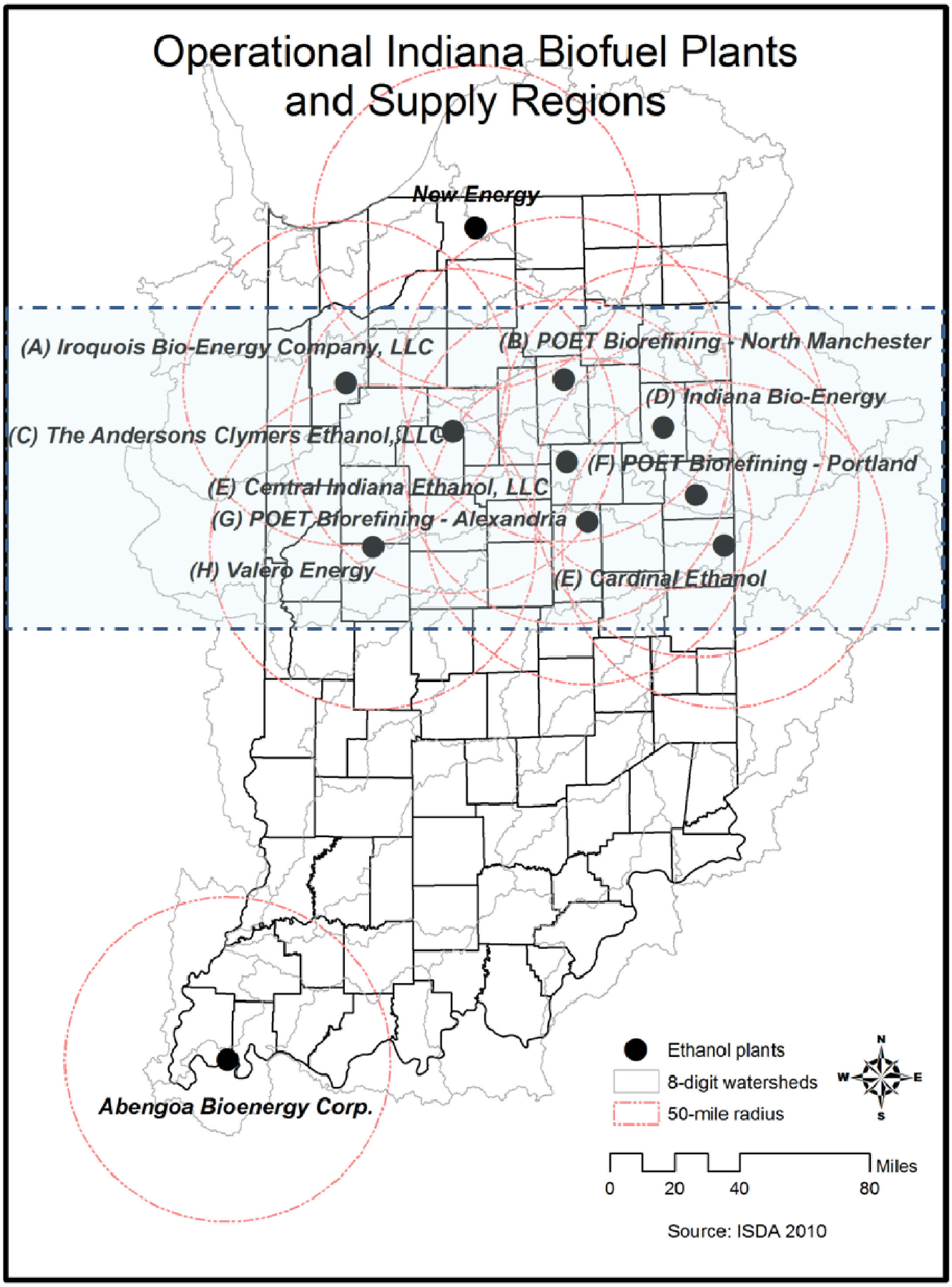

Figure 1. Corn-based ethanol plants in Indiana and the site selection for water use regime construction based on their relative distances. Blue highlighted area represents the geographic area within which the hydrogeologic characteristics are expected to be similar.

Primary Findings

Water-use regime plots were generated for all of the watersheds evaluated, and will be included in a research publication that is being currently prepared. Here, we present some representative plots for the Salamonie watershed (Figure 2) to illustrate the water-use regimes, and summarize the primary findings based on similar analyses in all other watersheds.

1. Given the humid climate and because crop irrigation is not a dominant demand, water regime plots at the *watershed scale* suggest minimum freshwater stress at the annual or even monthly time scales under *average* weather conditions. That is, consumptive uses of freshwater withdrawals by major sectors (utilities and industries) are small (even the maximum h_{out} is less than 0.1, which means no stress according to criticality ratio). Note that the data points lie on or close to the 1:1 line (withdrawals ~ return flows).
2. This evaluation, however, changes dramatically when *water-quality impairment* is accounted for in construction of the water-use regime plots; all watersheds we evaluated would be judged to be under severe water stress. Here, we considered water quality impairment from non-point sources. Stream concentrations of the herbicide atrazine exported from watersheds (based on % area planted to corn) was used to represent surface water quality impairment.
3. We have assumed that pollutant discharges from point sources (e.g., industrial operations, including biorefineries) meet all regulatory standards such that water quality is above acceptable thresholds for human and ecological health. However, further research is needed to establish that our assumption is indeed valid.
4. Under *drought conditions*, all watersheds we examined would be judged as being under severe stress both from quantity and quality perspectives. In case of Salamonie watershed, the water stress in summer season increased beyond 0.2 (mid-stress) and reached 0.45 (high-stress) in August.
5. Competing demands for freshwater are most likely to be experienced at spatial scales smaller than a watershed scale. That is, at a township or community level, freshwater demands from multiple sectors would be a significant issue as new demands from biorefineries are added. This is especially important since freshwater withdrawals are from groundwater sources, but return flows are to surface waters (streams). Thus, continued depletion by increasing pumping from aquifers can, over time, result in significant water stress at the local level.
6. Freshwater use data we utilized in our analysis came from USGS reports which are published once every five years and are available aggregated only at the county level. We did not access data that might be available with the local authorities who issue permits for groundwater use. Our assessments would be enhanced if such local-scale data were used to generate the water regime plots, and these plots would be even more useful to local water managers.
7. With likely changes in rainfall patterns [e.g., increasing probability of intense extreme events of floods and droughts], increasing competition for freshwater resources is expected. As such, careful assessment of shifting water-use regimes [increased stress] is needed in water allocation decisions.

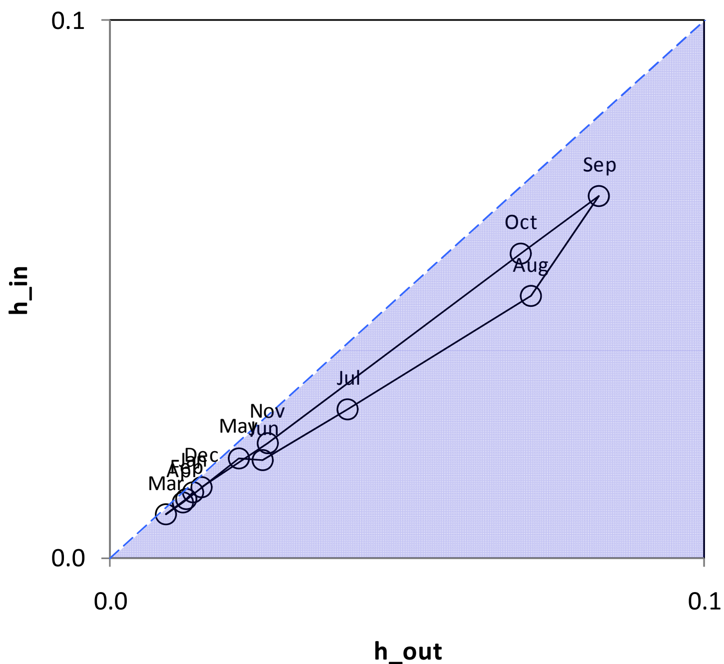

Figure 2A. Monthly variation of water use regime in mean weather condition <u>without the consideration of water quality.</u>

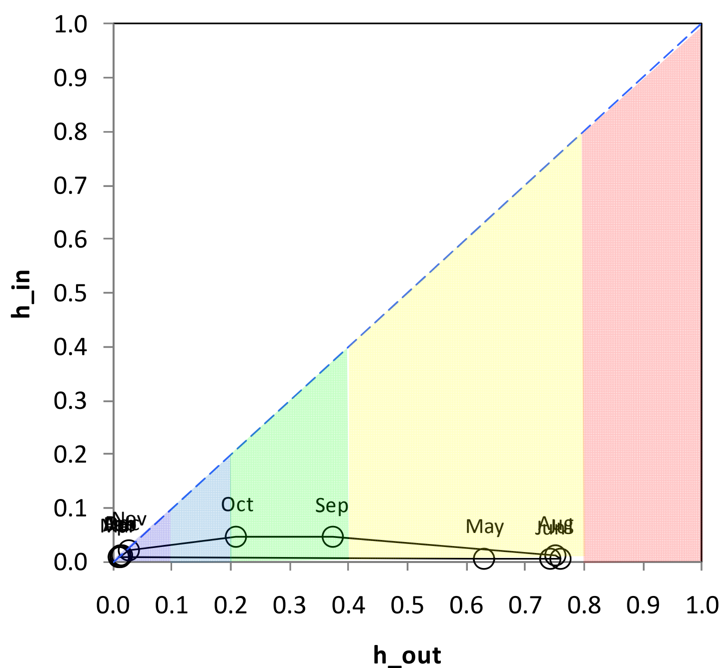

Figure 2B. Monthly variation of water use regime in mean weather condition <u>with the consideration of water quality</u>

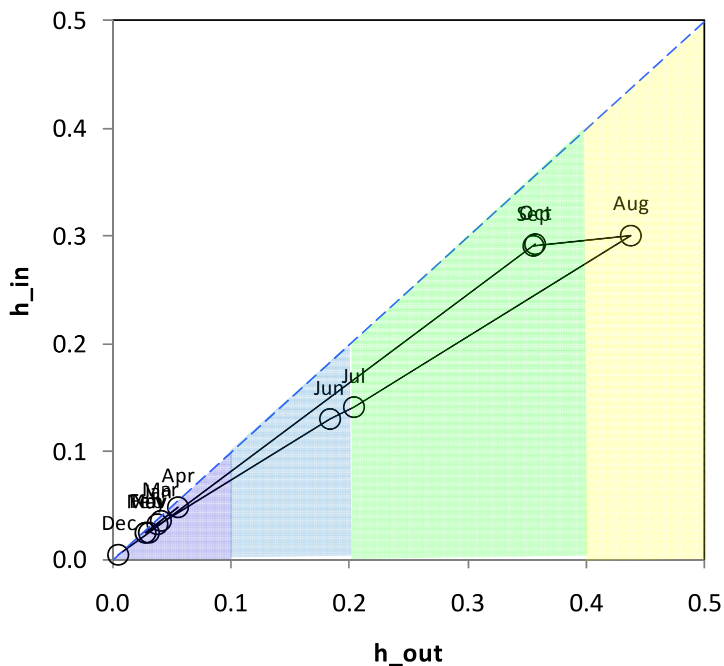

Figure 2C. Monthly variation of water use regime <u>under extreme drought condition without the consideration of water quality</u>

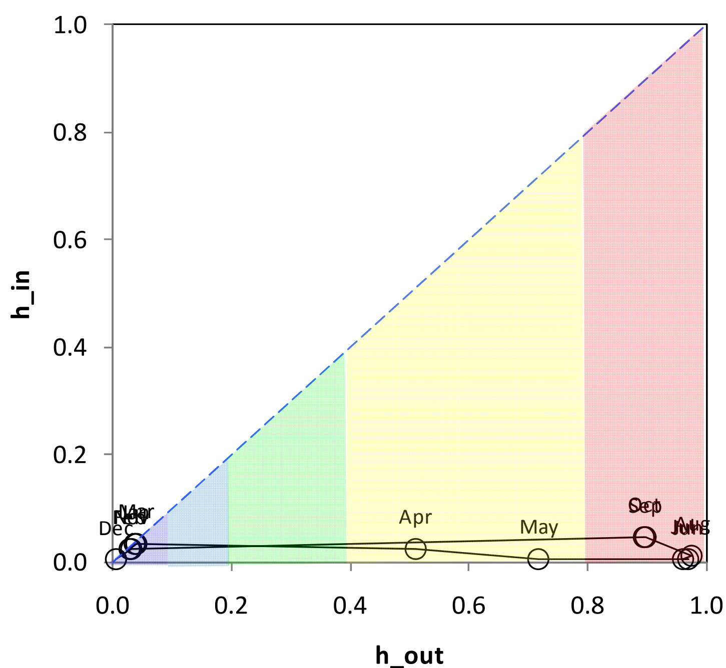

Figure 2D. Monthly variation of water use regime under <u>extreme drought condition with the consideration of water quality</u>

Practical Implications

Current water-use status of biofuel refineries located in several watersheds within central Indiana was evaluated. Our results will provide an assessment tool as well as critical information to local governments and water management authorities to: (1) assist successful decision making on selecting which biomass conversion technology should be adopted, (2) where to locate these technologies in terms of minimizing local and regional impact on fresh water resources; and (3) plan sustainable expansion of biofuel production to reach overarching goals of energy independence.

Graduate Student training

This project was lead by Mr. Jeryang Park (CE PhD), mentored by Professor Suresh Rao (CE). Mr. Parks' PhD dissertation topic focuses on modeling resilience of biofuel production systems, and the dynamics of coupled industrial systems (biorefineries) and natural systems (biomass production; water resources). His research will examine adaptive strategies needed to promote sustainability of biofuel production under volatile (i.e., stochastic forcing & feedbacks) of climate and markets. Mr. Park assisted Professor Rao in teaching the Global Water Resources Sustainability (CE597), a graduate course taught during spring 2010 semester. This inter-disciplinary course had an enrollment of about 15 graduate students, derived from engineering, agriculture, and liberal arts programs. The class included several students from the Ecological Science and Engineering Inter-disciplinary Graduate Program (ESE-IGP). Initial parts of this study (e.g., data gathering; conceptual model development, etc) were conducted as a class project within this CE597 course. Mr. Park led a group of the following students to compile the data, and develop the preliminary assessment: Carson Reeling (M.S. student; Agricultural Economics Department); Elizabeth Cox (M.S. student; ESE-IGP); Ryan Hultgren (senior; Civil Engineering), Kasey Faust (M.S. student; Civil Engineering). Mr. Reeling played a key role throughout the project period in working with Mr. Park and Dr. Rao to compile the data, complete the data analyses, and generate the final report.

Graduate Student Evaluation [Carson Reeling]

In the spring of 2010, I enrolled in Dr. Rao's class, "Water Resources and Sustainability." My training is in agricultural economics, but having been born and raised in the high desert of Eastern California, I am particularly interested in water resource management. I was therefore very happy to find a class in water resource management that, despite being taught in the civil engineering department, was highly accessible to students of different backgrounds.

A requirement of the class was to develop a term project that explored some component of water resource sustainability. Dr. Rao and his graduate student, Jeryang Park, presented me and other classmates with the opportunity to satisfy this requirement by contributing to the research project supported by your grant. I believed that the project had the potential to be both challenging and successful, so I chose to participate.

Having worked on the project over the course of spring semester, my initial assessment proved to be correct. The project challenged me to expand my academic horizon beyond economics and into the physical sciences. While previously only economic considerations seemed relevant, analyzing the basic hydrology behind biofuel plant location decisions and the effects of agricultural production on water quality taught me the value of expanding my perspective to take a more systems-oriented approach to researching environmental issues.

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LANDSCAPE CONTROLS ON RIPARIAN ZONE FUNCTION VIS-À-VIS MULTIPLE CONTAMINANTS AND ASSOCIATED POLLUTION TRADE-OFFS

Basic Information

Title:	LANDSCAPE CONTROLS ON RIPARIAN ZONE FUNCTION VIS-À-VIS MULTIPLE CONTAMINANTS AND ASSOCIATED POLLUTION TRADE-OFFS
Project Number:	2010IN244B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	6
Research Category:	Water Quality
Focus Category:	Hydrogeochemistry, Toxic Substances, Geomorphological Processes
Descriptors:	
Principal Investigators:	

Publications

There are no publications.

Title: Landscape controls on riparian zone function vis-à-vis multiple contaminants and associated pollution trade-offs.

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Abstract / Summary

Riparian zones (near stream zones) are frequently used as best management practices to reduce nitrate transport to streams in agricultural areas. Nevertheless, research has shown that the high organic matter content of riparian zone soils and the reducing conditions usually observed in riparian systems can release large amount of phosphorus, methylmercury, and greenhouse gases (GHG) (CO_2, N_2O, CH_4) in the environment. These elements/molecules (P, Hg, CO_2, CH_4, N_2O) are major environmental contaminants and the interconnections among P, Hg, C, and N cycling in riparian systems must be better quantified/understood in order to wisely integrate riparian zones into water quality improvement strategies without negatively augmenting P and Hg release to surface waters, or GHG emissions to the atmosphere. The goals of this project are threefold: 1) determine the complex interactions between N cycling, P sorption/desorption, Hg accumulation, MeHg production and greenhouse gas (CO_2, CH_4, N_2O) production/consumption in riparian ecosystems; 2) determine to what extent landscape hydrogeomorphic characteristics (HGM) (topography, soil, surficial geology) can be used to predict N removal, P sorption/desorption, Hg accumulation, methylmercury production and GHG production/consumption in riparian ecosystems; and 3) collect preliminary data for the development of larger proposals. Funding this proposal will also allow the PI to develop a new international collaboration with Dr. Carl Mitchell (University of Toronto, Canada; see letter of collaboration) and to further develop his skills in watershed biogeochemistry/hydrology by incorporating Hg, a contaminant of national importance, into his research on N, P and C cycling in the environment. In addition to presenting results at national conferences (AGU, GSA, SSSA), the PI and students involved in the project will also present research results at local conferences such as meetings of the Indiana Academy of Science and Indiana Water Resources Association, and the regional meeting of the Geological Society of America.

Problem:

The atmospheric trace gases carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) play important roles in the chemistry and energy balance of the earth's atmosphere, and increases in the concentration of these greenhouse gases (GHG) in the atmosphere has been linked to climate warming. Preliminary data collected by the PI and others suggest that riparian zones may be extremely large contributors of GHG relative to the surrounding landscape (Jacinthe et al. unpublished data). Nevertheless, we have limited knowledge of the dynamics of GHG production and emission from riparian zones as there is a surprising imbalance between the large amount of research on N removal carried out in riparian zones and the lack of data on GHG production in these ecosystems.

Excess phosphorus in freshwater systems has been linked to eutrophication and the United States Environmental Protection Agency (USEPA) has identified P pollution as the greatest impediment to achieving water quality goals stated in the Clean Water Act. Although riparian zones sometime act as a phosphorus sink, they can act as a source as well. Understanding the conditions that regulate P sorption/release in riparian systems is therefore critical to best use riparian zones to improve water quality.

Mercury is another contaminant of national concern for water quality whose fate in the environment is significantly impacted by wetlands and riparian zones (Evers et al., 2007). Reduced conditions in many riparian zones allow sulfate reduction to take place, which is a critical step toward the production of methylmercury (MeHg). MeHg is readily bioavailable, more soluble than inorganic forms, and bioaccumulates in the food chain. A better understanding of how riparian zones and wetlands regulate Hg transport to streams and MeHg production is therefore critical to identifying major sources of Hg contamination in the landscape, and ultimately to better manage riparian zones and wetlands to achieve complex multi-contaminant water quality goals. **Is the promotion of riparian zones as best management practices for nitrate removal done at the expense of air quality (greenhouse gas production), or at the expense of water quality vis-à-vis mercury and/or phosphorus?**

Another key element to intelligent water and air quality management that utilizes riparian zones is the development of strategies to optimize riparian zone placement and conservation in order to achieve multiple water quality goals at the watershed scale. The distribution of organic matter in riparian soils and the variability of soil redox conditions spatially and temporally over a 12-month period is extremely difficult to assess directly over large scales (Gold et al., 2001). Much research has therefore been conducted in the past decade to identify landscape attributes capable of predicting N removal in riparian zones without directly measuring denitrification or N concentration in the subsurface (Gold et al., 2001). **Research indicates that topography, upland contributing area, upland aquifer size, surficial geology, and soil texture can be used as indicators of riparian zone hydrological functioning (moisture content, water table dynamics, flow path, magnitude of nutrient inputs to the riparian zone) and to some extent as indicators of the biogeochemical conditions regulating N removal in riparian soils (aerobic vs. anaerobic, N removal, occurrence of denitrification).** This approach has, however, not yet been widely applied to biogeochemical processes regulating P, Hg and GHG in riparian zones. Very recent research nevertheless suggests that similar hydrogeomorphic analyses can be applied for making improved estimates of MeHg production and/or GHG fluxes in riparian systems (Vidon USDA grant, in progress). **Overall, research therefore suggests that landscape hydrogeomorphic characteristics can be helpful in generalizing riparian zone functions for entire watersheds.** Being able to generalize riparian zone function at the landscape scale and to determine to what extent landscape hydrogeomorphic characteristics can be used to predict the role of riparian zones vis-à-vis multiple contaminants (i.e. N, P, Hg, MeHg, CO_2, N_2O and CH_4) is a critical step toward developing better estimates of the aggregate role of riparian zones as water quality buffers.

Research Objectives:

1) **Determine the complex interactions between N cycling, P sorption/desorption, Hg accumulation, MeHg production and greenhouse gas (CO_2, CH_4, N_2O) production/consumption in riparian ecosystems**. To what extent are the processes regulating the fate of these elements/molecules in riparian zones and wetlands mutually exclusive? Are we trading water quality with respect to N at the expense of air quality (CO_2, CH_4, N_2O production) or water quality vis-à-vis other water contaminants of national importance (P, Hg)?

2) **Determine to what extent landscape hydrogeomorphic characteristics (HGM) (topography, soil, surficial geology) can be used to predict N removal, P sorption/desorption, Hg accumulation, methylmercury production and greenhouse gas (CO_2, CH_4, N_2O) production/consumption in riparian ecosystems**. Research has shown that HGM characteristics can be used to successfully predict N removal via denitrification in riparian systems and that biogeochemical conditions regulating N fate in riparian systems also regulate P, Hg and GHG dynamics. However, little is known about the extent to which HGM characteristics can be used to simultaneously predict P, Hg and GHG dynamics in riparian systems or whether certain characteristics are better predictors for individual processes. Determining how landscape HGM characteristics can be used to predict P, Hg and GHG dynamics in riparian systems is critical in order to optimize the use of riparian zones as best management practices in a world where developing strategies to mitigate the impact of anthropogenic activities on environmental quality vis-à-vis multiple contaminants is more and more important.

Methodology:

We used three riparian zones with contrasting hydrogeomorphic characteristics. These sites are currently used as part of USDA grant # 2009-35112-05241 ($400K) where Vidon and others look at greenhouse gas production across a range of HGM characteristics common in the US Midwest. Access to the sites has therefore already been granted to the PI and will continue at least until 2012 (completion of USDA project). The first site **(Leary Weber Ditch** or **LWD site)** represents the most common type of riparian zones in central Indiana and in artificially drained landscapes of the Midwest in general. It corresponds to the numerous narrow riparian zones (20-30 m wide) found downslope from drained agricultural fields dominated by corn and soybean crops and located near streams that have been artificially deepened and straightened. The second site (**Scott**

Starling site or **SS site**) corresponds to riparian zones found at the outlet of first and second order streams in deep (15-20 m) and wide river valleys (100-200 m) in glacial till landscapes. Outwash deposits and shallow layers of alluvium (1-2 m) are often found in these deeply incised glacial valleys. Land use in the adjacent upland is generally dominated by managed forest and low density residential housing development. The third site (**White River site** or **WR site**) corresponds to large riparian zones (100-200 m wide) located along 3rd and 4th order streams where outwash and/or large deposits of alluvium have accumulated since the last glacial maximum. Soils at the site are generally well drained but are subject to large water table fluctuations and flooding in response to changes in water levels in the adjacent river. Land use in these large floodplains is generally dominated by agriculture with corn and soybean as the dominant crop types. Further, **both the WR and the SS sites contain wetland areas associated with topographic depressions at each site.** We will capitalize on the occurrence of these wetland areas at each of these sites to document variations in N and Hg cycling processes at these locations and offer a greater spectrum of HGM characteristics/hydrological conditions.

Using groundwater wells (for water level and water quality sampling) and static chambers (for GHG monitoring) already in place at the sites (as well as piezometers to be installed upon funding of this proposal), we monitored GHG emissions and water quality over a 12-month period. Water samples in wells and piezometers were collected approximately once a month over a 12-month period, plus immediately after selected precipitation events, as it is expected that significant changes in water quality and/or GHG emissions may be observed at the sites in the days following precipitation events owing to quick changes in water table levels and nutrient/contaminant inputs to the sites as overland flow, stream over-bank flow, or subsurface flow occur. Each water sample was analyzed for the following: temperature, dissolved oxygen (DO), redox potential (Eh), and dissolved organic carbon (DOC), nitrate, ammonium, chloride, Hg, MeHg, sulfate and phosphate concentrations. Temperature, DOC, DO and Eh allowed us to characterize differences in key fundamental biogeochemical characteristics between sites and between locations within each site. Nitrate concentration and changes in nitrate concentration along subsurface flow paths within each riparian zone (along each transect) allowed us to measure nitrate removal efficiency at the sites. Chloride, a naturally occurring conservative tracer in the subsurface, allowed us to determine the importance of dilution in N removal at each site (Altman and Parisek, 1995). Total mercury (Hg) and MeHg concentration allowed us to determine Hg storage and MeHg production at each site (Mitchell et al., 2008). Sulfate (associated with MeHg production) and phosphate concentration in the subsurface allowed us to identify whether sulfate removal/consumption is occurring and whether the site is a P sink or a P source (Carlyle and Hill, 2001). These simple measurements allowed us to identify subsurface biogeochemical conditions / water quality and the extent to which key processes regulating N, P and Hg dynamics co-occur at the sites. All samples were analyzed using standard methods as outlined in Clesceri et al. (1998) and Jacinthe and Dick (1997).

Results

All samples have been collected at this time and are currently being analyzed. Data analysis is underway and it is expected that preliminary results will be available in Fall 2011.

Major Conclusions and Significance

No major conclusions have been established at this time; however, we expect results generated by this project to be highly significant for the following reasons:

The proper management of riparian zones at the watershed scale requires the development of strategies to identify best riparian zone placement strategies at the watershed scale to optimize water quality vis-à-vis nitrogen without creating air quality problems or other water quality problems with respect to other contaminants such as P or Hg. Linking N, P, Hg, and GHG dynamics to easily measurable landscape characteristics such as topography, soil texture or surficial geology is a critical step toward the development of riparian zone placement strategies to achieve multiple water quality goals at the watershed scale. **With this project we expect to develop a new conceptual framework based on landscape hydrogeomorphic characteristics to determine where to best place or maintain riparian zones for optimal environmental benefits vis-à-vis multiple contaminants (P, N, Hg, GHG).**

Publications

Vidon, P, 2010. Wetlands, riparian zones, stream restoration and environmemtal conservation in the Northeast: Do we really understand what we are doing? **Northeastern Ecosystem Research Cooperative Conference**, Saratoga Springs, NY, November 2010.

Grant Submissions:

NAME (List/PD #1 first)	SUPPORTING AGENCY AND AGENCY ACTIVE AWARD/PENDING PROPOSAL NUMBER	TOTAL $ AMOUNT	EFFECTIVE AND EXPIRATION DATES	% OF TIME COMMITTED	TITLE OF PROJECT
Vidon	SUNY-ESF Seed grant Program (State funding)	$8,000	05/11-04/12	5%	Riparian zones as best management practices: a double edge sword for environmental quality
	Pending:				
Vidon, P., Walter T.	USGS- National Institute of Water Resources (#2011NY167G) (Federal Funding)	$249,334	9/1/11-8/31/14	10%	Optimizing Riparian Zone Placement strategies to increase environmental benefits toward multiple contaminants.
Vidon, Groffman, Gold, Kellogg, Addy	USDA-NIFA-AFRI (#TBD)	$500,000	05/12-04/15	10%	Landscape controls on water quality and greenhouse gas emission in riparian zones of the US Northeast

Students

One graduate student

Transport and fate of pharmaceutical compounds in an Indiana stream

Basic Information

Title:	Transport and fate of pharmaceutical compounds in an Indiana stream
Project Number:	2010IN251B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	9
Research Category:	Water Quality
Focus Category:	Acid Deposition, Water Quality, Toxic Substances
Descriptors:	
Principal Investigators:	Todd V Royer

Publications

There are no publications.

Title: Transport and fate of pharmaceutical compounds in an Indiana stream

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Abstract / Summary:

Pharmaceutical and personal care products (PPCPs) have been documented throughout the surface waters of the United States, but many questions remain regarding the fate and transport of PPCPs in streams. The primary point source of these contaminants in the environment is effluent from wastewater treatment plants (WWTP). The purpose of this study was to investigate behavior of PPCPs downstream of a WWTP and assess the impact of wastewater discharge on a small stream. The study was conducted on Jack's Defeat Creek in Monroe County, Indiana. Five sites, including one upstream of the WWTP, the effluent, and three downstream of the WWTP outfall, were sampled for PPCPs and nutrients in November 2010 and February 2011 using a Lagrangian sampling approach. The upstream site displayed low PPCP concentrations relative to the downstream sites. The effluent samples contained the greatest concentration of PPCPs, and the downstream sites had lower concentrations of PPCPs than did the effluent, due to dilution. No significant decline in PPCP concentrations was found in the 500-m reach downstream of the WWTP outfall. The discharge of treated effluent resulted in increased concentrations of dissolved nutrients (nitrogen and phosphorus) downstream of the WWTP outfall, which in turn supported a thick biofilm community. Despite the biological activity in the stream, there was no evidence of attenuation or biodegradation of PPCP over a 500-m reach of stream.

Problem:

Understanding the extent to which streams can naturally attenuate pharmaceutical and personal care compounds is critical to water resource management; however, little information exists on the transport and fate of these compounds in streams.

Research Objectives:

The objectives of this project are to (1) document patterns in transport and attenuation of individual pharmaceutical and personal care products (PPCPs) in Jack's Defeat Creek (Monroe County, IN) downstream from a WWTP outfall; (2) determine the fraction of attenuation that is due to dilution vs. true removal from the water column; (3) provide an initial measure of seasonal variation in PPCP transport and attenuation.

Methodology:

Site description – Jack's Defeat Creek flows through the town of Ellettsville, IN (population ~ 6400) and receives effluent from the town's waste water treatment plant

(WWTP). The Ellettsville WWTP has a design capacity of 2.3 million gallons per day and it is the only NPDES-permitted point source to Jack's Defeat Creek. UV disinfection is used from April to October, and therefore was not in use sampling for this study. The drainage area above the study reach is approximately 40 km^2 with 47% forest, 39% agriculture/grass/pasture, and 14% urban.

Water Sampling – Releases of salt (NaCl) were used to measure flow times and establish several sampling transects with in the 550 m reach of Jack's Defeat Creek downstream from the WWTP outfall. Stream discharge was measured by hand using the velocity-area method and daily effluent discharge was reported by the Ellettsville WWTP. Samples for dissolved organic carbon and nutrients were collected at the same transects as the PPCP samples. Grab samples were collected in sterilized 900 mL amber bottles and filtered immediately at a "clean" station 50 meters from the stream. Filtered samples were placed immediately on ice and stored in the dark. Distilled, de-ionized water was used for field blanks. In November, one sample was collected from the effluent and 2 replicate samples were collected 25m, 150m, 225m, 32m5, and 510m downstream downstream from the WWTP outfall. In February, samples were collected from 25m upstream of the WWTP outfall, and 25, 150, and 510 meters downstream. Sampling was conducted from late morning to afternoon on November 21, 2010 and February 13, 2011. Personnel refrained from the use of personal care items, tobacco, and caffeine during, and for 12 hours prior to, the sampling. Samples were delivered to Indiana State Department of Health on ice for analysis less than 24 hours after collection.

Results:

Downstream of the WWTP, the stream was nutrient-rich and contained a well-developed biofilm during both sampling dates. There was less than 2.5 cm of rain from August until the November 21st sampling, as a result the WWTP effluent provided more than half of the flow in Jack's Defeat Creek in November 2010. Contrary to the November sampling, the flow in February was about 4 times greater than the effluent contribution from the WWTP. Stream discharge was 60 L/s in November and 223 L/s in February. The WWTP effluent discharge was 33 L/s in November and 46 L/s in February.

Although DEET was quantified in all PPCP samples (including blanks), due to analytical concerns and inconsistencies, results for DEET were considered unreliable and thus are not presented or used in any mass balance calculations. No PPCPs were detected in sample blanks, indicating that contamination was not introduced during sample collection or filtering. In November, caffeine, carbamazephine, cotinine, gemifibrozil, naproxen, triclocarban, sulfamethoxazole, and trimethoprim were present in all samples of stream water. All of these compounds occurred in the WWTP effluent, except for caffeine which was not detected in the effluent. Caffeine in the stream water apparently originated from upstream, non-point sources. During the February sampling, acetaminophen, carbamazephine, cotinine, gemifibrozil, triclocarban, sulfamethoxazole, trimethoprim, and tylosin were present in the stream samples (Figure 1).

In November, sulfamethoxazole contributed to more than 75% of the total PPCP concentration in the effluent with trimethoprim accounting for most of the remaining concentration. In February, carbamazephine, gemifibrozil, sulfamethoxazole, and trimethoprim comprised more than 95% of the total PPCP concentration in the effluent. There are clear indications of seasonality in the PPCP data, suggesting an important role of hydrologic variability as well as variability in the types and amounts of compounds used by the population served by the WWTP.

The majority of the PPCPs had a relatively low concentration upstream, a high effluent concentration, and consistent downstream concentrations with no evidence of attenuation. Combining the concentration of each PPCP into a total PPCP concentration illustrates the role of the WWTP and the lack of downstream attenuation (Figure 2). We used the concentration and discharge data to calculate the load of total PPCPs in the effluent and the in the stream at 150m downstream of the WWTP outfall. In November, the effluent load was 74 µg/s and the load at 150m was 76 µg/s. The loads in February were 127 µg/s and 132 µg/s in the effluent and 150m station, respectively.

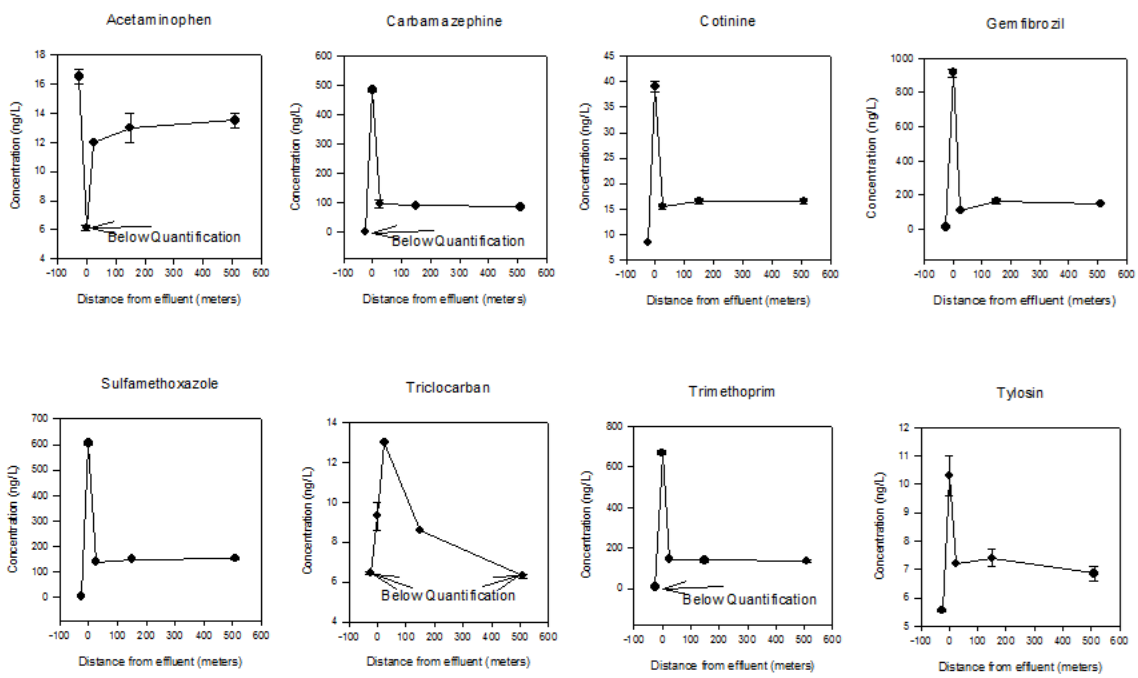


Figure 1. PPCPs that occurred at or above detection level in Jack's Defeat Creek near Ellettsville, IN on February 13, 2011. Symbols represent the average of two duplicate samples at each distance (-25, 0, 25, 150, 510m) from the WWTP outfall. The -25m distance represents a location 25m upstream of the outfall. The bars show the values of the two duplicate samples.

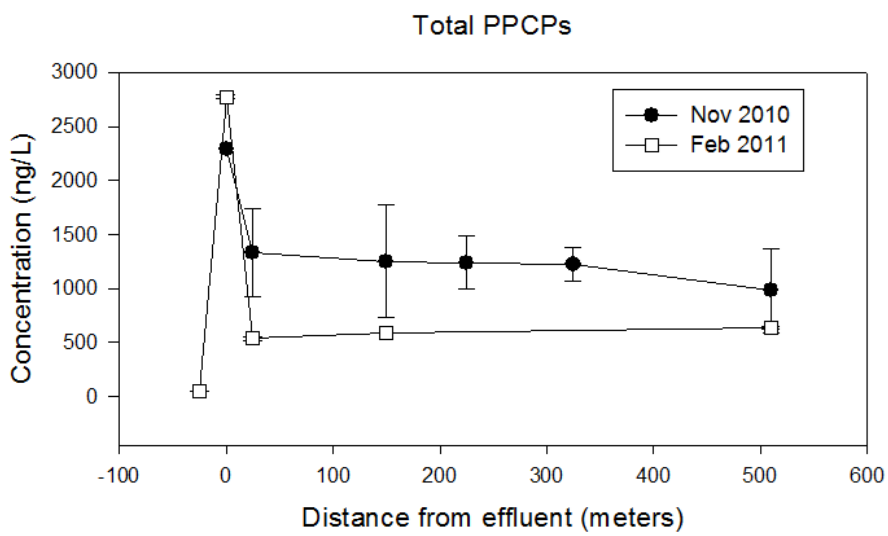


Figure 2. The concentration of total PPCPs in Jack's Defeat Creek in relation to the Ellettsville, IN WWTP outfall on November 21, 2010 and February 13, 2011. The 0-m location indicates a sample of the effluent.

Major Conclusions and Significance:

Pharmaceutical and personal care products (PPCPs) are ubiquitous in aquatic systems but questions remain regarding the toxicology of many PPCPs and their effects on aquatic ecosystem function. It is critical to understand how these compounds behave upon entering the aquatic environment. This study found that PPCPs entering a small stream from a WWTP outfall were not attenuated during transport through a 500 m reach of the stream, even though the stream was shallow and contained well-developed biofilms. This suggests that PPCPs could be transported long distances from the input source. Long distance transport has implications for downstream drinking water supplies, such as reservoirs and larger rivers. Additionally, the results suggest small but consistent input of PPCPs from non-point sources upstream of the WWTP.

Publications/Presentations:

Looper, E.N., A.B. White, and T.V. Royer. Transport and fate of nutrients and pharmaceutical compounds in a stream receiving effluent from a wastewater treatment plant. Oral presentation, June 2, 2011. Indiana Water Resources Association Conference, Muncie, IN.

Grant Submissions: No grants have been submitted yet, although a proposal is being developed.

Students Involved with the Project: Two students were involved with the project, one graduate student (Andy White, MS in Environmental Science) and one undergraduate student (Erin Looper, BS in Environmental Science).

Using Remotely Sensed Data in Combination with Ground Level Geochemistry to Evaluate Continued Impacts of Acid Mine Leakage on Abandoned Mine Lands

Basic Information

Title:	Using Remotely Sensed Data in Combination with Ground Level Geochemistry to Evaluate Continued Impacts of Acid Mine Leakage on Abandoned Mine Lands
Project Number:	2010IN302B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	8
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Sediments, Water Quality
Descriptors:	
Principal Investigators:	Jennifer C Latimer, Jagadeesh Anmala

Publications

There are no publications.

Using Remotely Sensed Data in Combination with Ground Level Geochemistry to Evaluate Continued Impacts of Acid Mine Leakage on Abandoned Mine Lands

Project Id: 2010IN302B
Title: Using Remotely Sensed Data in Combination with Ground Level Geochemistry to Evaluate Continued Impacts of Acid Mine Leakage on Abandoned Mine Lands
Project Type: Research
Start Date: 3/01/2010
End Date: 2/28/2011
Congressional District: 8
Focus Categories: Geochemical Processes, Sediments, Water Quality
Keywords: Acid Mine Drainage, Abandoned Mine Lands, Biogeochemistry
Principal Investigators: Latimer, Jennifer C

Abstract / Summary

Many abandoned mine lands continue to cause significant environmental concerns, particularly those that were abandoned prior to state and federal laws governing reclamation. The abandoned Friar Tuck Mining Complex (FTMC) in Greene and Sullivan counties in Indiana continues to impair local water quality despite closing in 1952 for operations and multiple remediation attempts. Many areas within the Friar Tuck Mining Complex have been successfully reclaimed; however, the area of research interest continues to be impacted by runoff from gob piles and acidic drainage. Subsequently, many areas are characterized by a loss of vegetation and the exposure of bare soil. These areas are of particular concern because contaminated soil may leave the site during summer months as aerosols due to soil desiccation and are more likely to be transported off site during runoff events. The primary goal of this project was to evaluate spatial variability in the distribution of metals in surface soils and to evaluate how the areas of bare soil have changed over time using remote sensing data. In May 2010, 258 soil samples were collected at FTMC to evaluate metal accumulation and bioavailability using several different geochemical techniques, including bulk geochemistry following reaction with water and acid and a sequential extraction technique. Results indicate that surface soils at FTMC continue to have low pH (pH=4-1), and surface soils have elevated concentrations of bioavailable metals such as Zn, Cu, Cr and Pb. Evaluation of the remote sensing data is ongoing.

Problem: Because Indiana is seventh in the nation for coal reserves, followed by Illinois, exploiting these coal resources through mining will continue for some time. Indiana continues to have impaired water quality as a result of AMD, and this will likely continue well into the future. Understanding the associations between different soil fractions and metal bioavailability is important when considering remediation plans. In addition, remotely sensed data may provide a more efficient means to identify sensitive areas.

Research Objectives:

1. Acid and water extractable metal concentrations following ashing (to remove organic matter content) were determined for all samples (~500). Samples analyzed by ICP-OES to estimate metal bioavailability.
2. Total metal concentrations were determined using microwave assisted attack by strong acids and analysis by ICP-OES.
3. Samples were evaluated using a sequential extraction technique (Tessier, 1979) to determine the sedimentary distribution of the metals: metals that are adsorbed or associated with oxides, carbonates, or organics, and residual metals. All samples were analyzed by ICP-OES.
4. The spatial distribution of metals for objectives 1-3 were determined by interpolating between data points and kriging the data (Fig. 1 and Fig. 2).
5. Remotely sensed data for the Friar Tuck mine complex, including the study area, was collected from the GeoEye-1 satellite and from a high resolution hyperspectral flight over the study area. The remotely sensed data is being used to identify sensitive areas and evaluate how these areas have changed over time.

Methodology: Surface soil samples were collected from FTMC in May 2010. Soil pH was determined in the field, and samples were brought back to the biogeochemistry laboratory at ISU and freeze dried. Freeze dried samples were then disaggregated and sieved. Samples were then treated using multiple geochemical techniques to evaluate metal bioavailability, including reaction with water, reaction with acid, and a sequential extraction technique to evaluate more specifically how the metals were bound in soil. In addition, satellite imagery from the GeoEye-1 satellite were acquired as well as high resolution hyperspectral data from a flight over the area in Fall 2010. The remote sensing data is being used to identify sensitive areas with the larger study area and to evaluate how areas of bare soil may have changed (i.e. size and extent) over time.

Results

The remote sensing work is still ongoing due to the lateness of actually receiving some of the data. The geochemical data illustrates that FTMC soils have elevated metals concentrations, some at the threshold effect and probably effect levels. Metals of particular concern are those that bioavailable, bioaccumulate, and have known deleterious effects, such as Pb, Zn, Cu, and Cd. From the sequential extraction, we also now can verify that most of the metals are associated with an oxide phase. In general, metal concentrations are highest in areas near seeps and surface flow.

Figure 1. Spatial Distribution of metals from the sequential extraction.

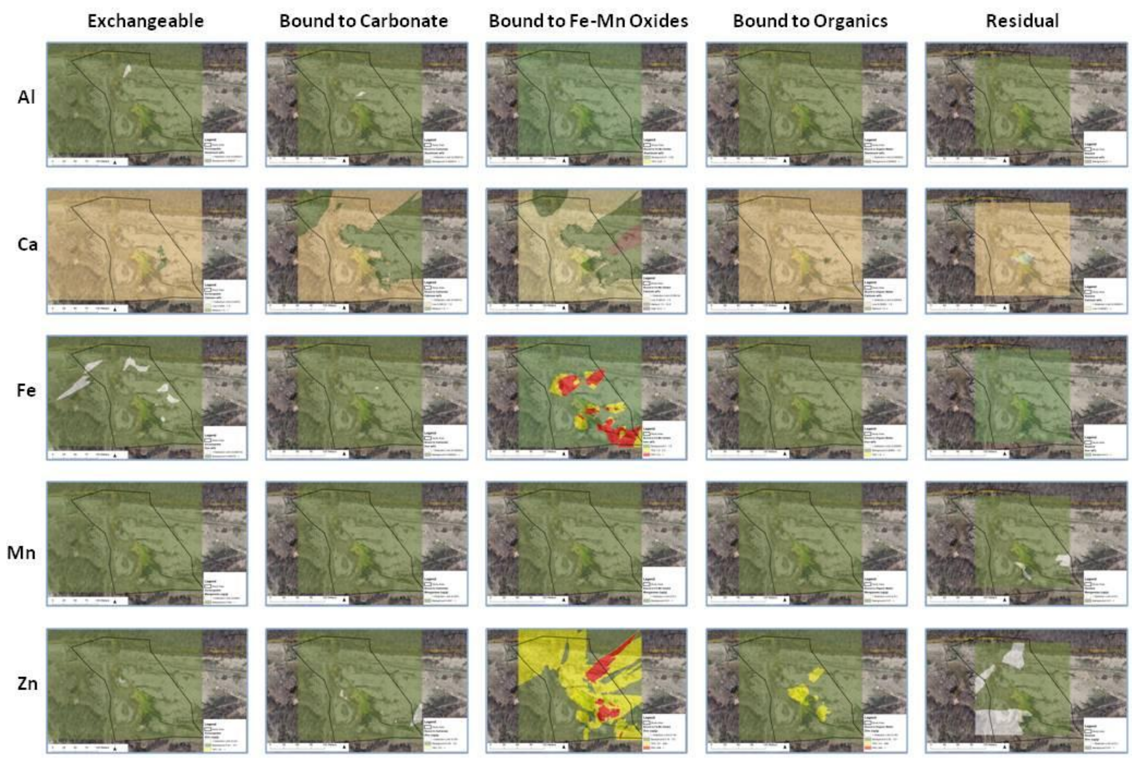
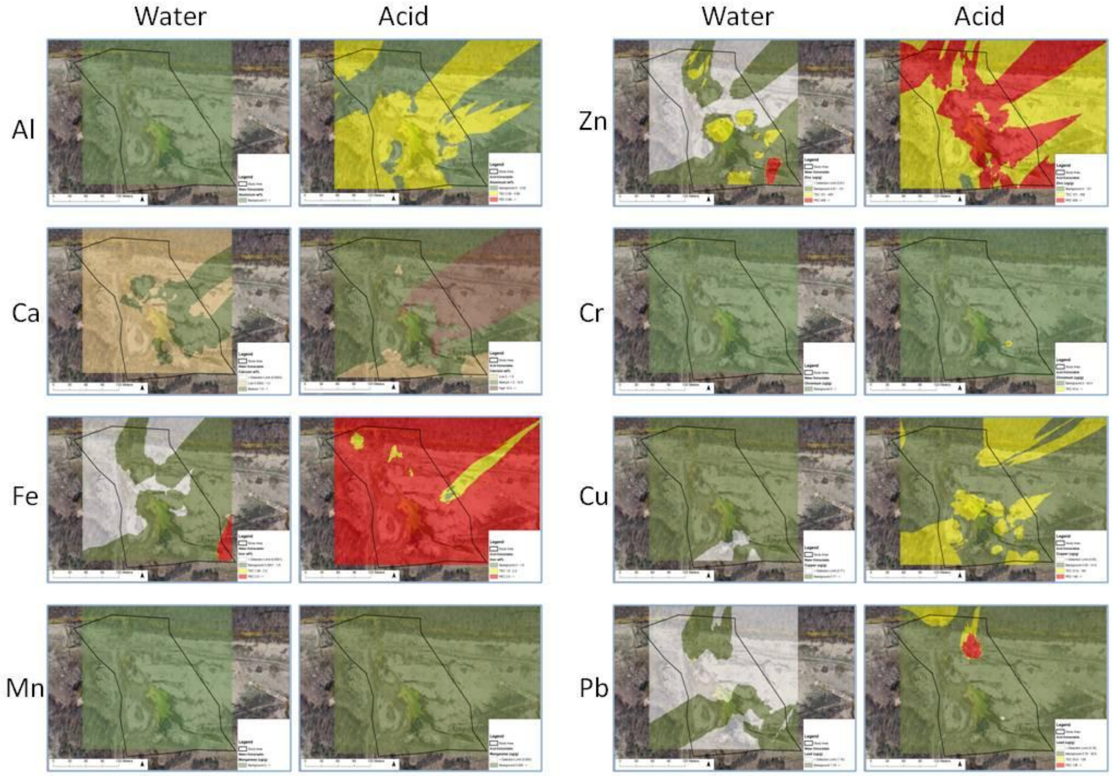


Figure 1. Spatial distribution of acid and water extractable metals.



Major Conclusions and Significance

Elevated bioavailable metal concentrations in the study area at threshold effect and probable effect levels likely pose a significant ecological risk. Bare soil, especially characterized by low pH and elevated metal concentrations, is likely to leave the site associated with runoff or aerosols and may be at least moderately bioavailable. In addition, elevated metals concentrations tend to be associated with areas of active seeps, surface flow, and areas with ponded water.

Publications

McBride, W.J., 2011. Assessing Environmental Conditions at the Friar Tuck Mining Complex, Dugger, Indiana. Master's Thesis, Indiana State University. (anticipated August 2011)

McBride, W.J. Latimer, J.C., Aldrich, S., Stacy, M.A., Terrell, N., Haldeman, B., 2010. Using a multi-proxy approach to evaluate environmental conditions at

the Friar Tuck Mining Complex, Dugger, Indiana. Geological Society of America Annual Meeting, Denver, CO, Abstracts with Programs.

Grant Submissions:

No major grants have been submitted yet; however, they at least one larger grant is expected to be submitted in the future.

Students

This project was the MS thesis of Windy McBride. Undergraduate students, Natasha Terrell, Brooke Haldeman, Katie Gritten, Heather Foxx, and Laura Majors have also been involved in the project. Another undergraduate student will likely continue working on the remote sensing part of the project during academic year 2011-12.

USGS Award No. G10AP00154 The Great Lakes Tributary Modeling Program 516(e): Purdue University and Michigan State University

Basic Information

Title:	USGS Award No. G10AP00154 The Great Lakes Tributary Modeling Program 516(e): Purdue University and Michigan State University
Project Number:	2010IN308S
Start Date:	9/7/2010
End Date:	8/31/2011
Funding Source:	Supplemental
Congressional District:	
Research Category:	Climate and Hydrologic Processes
Focus Category:	Sediments, Models, Management and Planning
Descriptors:	
Principal Investigators:	Bernard Engel, Bernard Engel

Publications

There are no publications.

General Report Format

Army Corps of Engineers 516(e): The Great Lakes Tributary Modeling Program
Work Plan for the Institute of Water Research (Michigan State University) and Purdue University

Report Format

Abstract / Summary

The Michigan State University Institute for Water Resources (IWR), in coordination with Purdue University, will develop four on-line water-quality management (sediment reduction) decision support systems for four priority watersheds identified by the U.S. Environmental Protection Agency as part of the Great Lakes Restoration Initiative:

- Saginaw River (Lake Huron - MI)
- Genessee River (Lake Ontario - NY)
- Maumee River (Lake Erie - OH)
- Fox River (Lake Michigan - WI)

The 2010-2011 project involves three main components: modeling, system design/development, and outreach/tech transfer.

Project Description

IWR will generate High Impact Targeting (HIT) models for each of the watersheds, utilizing the best available local data it can acquire. The HIT models will quantify erosion and sediment loading in each of the watersheds, and produce GIS layers identifying areas within fields where erosion and sediment loading is likely taking place.

The US Army Corps of Engineers (USACE) supported IWR and Purdue in the development of similar systems, Burns-Ditch/Trail Creek in 2007 and Swan Creek in 2009. The Swan Creek Watershed Management System (SCWMS) helps users identify and utilize tools to address agricultural and urban water quality issues in and around Toledo, OH. The proposed new systems for the Saginaw, Genesee, and Maumee watersheds will utilize the SCWMS as a template. For the Fox River watershed, IWR will develop a new interface that better integrates the tools of the SCWMS into a single mapping application. Through its success, the Fox River system could serve as a new decision support system template, readily expandable and scalable throughout the Great Lakes Basin.

IWR and Purdue will engage local partners in each of the watersheds to solicit user needs and feedback, and to facilitate technology transfer. In the Fox River, IWR and Purdue will conduct in-person hands-on training for users of the new system. In the other watersheds, IWR and Purdue will conduct webinars illustrating the new systems' utilities.

Research Objectives: Over the past decade, the Institute of Water Research (IWR), Purdue Agricultural and Biological Engineering Department, and the U.S. Army Corps of Engineers (USACE) have developed a strong working relationship through the Great Lakes Tributary Modeling Program. This relationship has yielded research on sediment loadings at multiple scales, GIS models for erosion and sediment loading risk, new and advanced modeling algorithms, multi-scaled prioritization maps, and on-line decision support systems to help users maintain and restore water quality in their watersheds. These achievements have been published in scientific journals, presented at numerous conferences, and disseminated through hands-on workshops. As a new decade begins, IWR and Purdue seek to strengthen the partnership with USACE by building on these earlier achievements to create new and more advanced decision support systems, faster and more efficient models, for broader geographic areas and larger, more diverse user-groups. The end result will be better tools in the hands of more decision makers, which will help keep more sediment on the land and out of the Great Lakes.

Results : Project is mid-term. None reported yet.

Major Conclusions and Significance Project is mid-term. None reported yet.

Publications: In the first two quarters of 2011 two webinar presentations were made, one to Corps of Engineers staff and one to the general public / stakeholder community. The webinar with stakeholders gained valuable insight to the path of development for the new tools.

Two Powerpoint™ presentations were made at Ann Arbor, at the Great Lakes Tributary Modeling Program 516(e) Annual All-Hands Meeting of the Corps of Engineers with the Great Lakes Commission.

Grant Submissions: None yet.

Students: Two graduate students and two undergraduates are working on various phases of this project.

Student	Program	Department
Youn Shik Park	PhD	ABE
Zhiwei Zhang	PhD	EAS
Karl Theller	BS	CS
David Tang	BS	CS

Information Transfer Program Introduction

None.

Plan Today For Tomorrow’s Flood: A Flood Response Plan for Agricultural Retailers

Basic Information

Title:	Plan Today For Tomorrow’s Flood: A Flood Response Plan for Agricultural Retailers
Project Number:	2010IN248B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	4
Research Category:	Water Quality
Focus Category:	Agriculture, Climatological Processes, Floods
Descriptors:	
Principal Investigators:	Fred Whitford

Publication

1. Whitford, F., S. Cain, J. Beaty, S. Hawkins, J. Southard, C. Henderson, S. Paddick, J. Bunte, J. Boger, B. Bellinger, S. Lambert, & K. Smith. 2010. Plan today for tomorrow’s flood: a flood response plan for agricultural dealers. PPP-87.

A. Titles: Publication

B. Focus Categories: AG, GW, LIP, NPP, SW, WQL, WS

C. Key Words: Pesticides, water quality, fish kill

D. Project Duration: March 1, 2009 to February 28, 2010

E. Funding Requested: 10,000

F. Principal Investigator: Fred Whitford, Ph.D., Coordinator, Purdue Pesticide Programs, Purdue University, 915 West State Street, West Lafayette, IN 47907-2054; Phone: 765-494-1284; Fax: 765-494-1556; Email: fwhitford@purdue.edu

Report Format

Problem:

We've all seen water levels in a creek rise and water ponding around the buildings after a steady rain of two hours. Farmers work around areas that flood by delaying planting productive "bottom land" until late spring to miss the heavy spring rains. Others living alongside rivers expect flooding, elevating their homes many feet above known flood levels. Experience teaches us to take floods seriously in those areas and to plan for the occasional flood. A flood is similar to a spill, fire, tornado, or any other emergency. But, floods often take longer in the recovery process because of hidden damages, and often, lack of insurance. Floods are a real risk that an ag retailer needs to consider and plan for as part of doing business. While we can't necessarily predict who will be impacted by the next flood, we can think about contingency plans to deal with floods.

Each flood has its own unique footprint over the impacted area and people's lives. How deep the water will be depends on the amount of water falling in that area, terrain, the elevation of the facility, the time period that it rains, how deep the river channel is, width of the flood plain, saturation level of rivers and creeks, and the ratio of impervious surface to soil surface. While each flood is different, plant managers know how their facility operates, and where chemicals are located in the warehouse. They know how water sheds off the property, how small rains impact the facility, and what roads are susceptible to flooding.

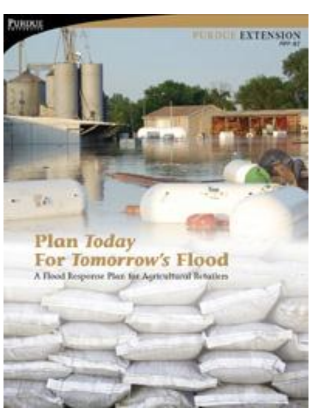
Relying on "Lady Luck" to get through the flood, or for that matter any emergency is a sure plan for disaster. Those who preplan and give some thought to what they would do in a flood usually can get back in business more quickly than those who did not put in place an action and reaction plan. How much you can accomplish will depend on how soon you start the process and how quickly the water is rising. The facts are clear: advance-planning limits the amount of damage caused by rising water levels.

Outreach/Extension Objectives:

Principal Deliverables:

Extension Publication

Whitford, F., S. Cain, J. Beaty, S. Hawkins, J. Southard, C. Henderson, S. Paddick, J. Bunte, J. Boger, B. Bellinger, S. Lambert, & K. Smith. 2010. When floods threaten (magnet). PPP-88.



Whitford, F., S. Cain, J. Beaty, S. Hawkins, J. Southard, C. Henderson, S. Paddick, J. Bunte, J. Boger, B. Bellinger, S. Lambert, & K. Smith. 2010. Plan today for tomorrow's flood: a flood response plan for agricultural dealers. PPP-87.

Accessibility on the Internet

http://www.ppp.purdue.edu/PPP_pubs.html

Purdue Press Release

Booklet Helps Agribusiness Prepare For, Recover From, Floods at http://www.purdue.edu/newsroom/outreach/2010/100608WhitfordPublication.html

eXtension Website

Publication converted into modules for nationwide audience in Cooperative Extension Service at http://www.extension.org/pages/33307/floods:-ag-retailers-flood-response-plan.

Use in 2010 Floods

Featured Item for Current Flood Problems at https://mdc.itap.purdue.edu/. Also searching internet under ag retailers flood eXtension, one can see that Extension and other publications around the country are referring to the publication in dealing with the 2011 floods. Putting the location of the publication on the goggle search engine, http://www.ppp.purdue.edu/Pubs/PPP-87.pdf, will show the wide appeal and distribution of the publication across the United States.

National Uses

Bill Hoffman, National Program Leader at USDA-NIFA shared it with large group of people, including the Under Secretary as an outstanding EDEN-type publication.

Indiana Presentations

A flood response plan for agricultural retailers. Indiana Water Resources Association. Columbus, Indiana.

A flood response plan for agricultural retailers. Purdue University Crop Management Workshops. Valparaiso, Bluffton, Brownstown, Vincennes, and West Lafayette, Indiana.

Publication Distribution

7,500 copies of PPP-were printed. Currently only 897 remain in inventory. Distribution was made to all pesticide coordinators in the country, to all agricultural cooperatives in the state, and any business licensed with the Office of Indiana State Chemist in Category 1. Many copies were sent to individuals at no cost upon request.

USGS Summer Intern Program

None.

Student Support					
Category	Section 104B Base Grant	Section 104G Competitive Grants	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	12				12
Masters	10				10
Ph.D.	1	1		2	4
Post-Doc.					
Total	23	1		2	26

Indiana Program 2010 report

Provided separately and late.

Notable Awards and Achievements

Publications from Prior Years